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RESEARCH ON MAGNESIUM ANTIMONIDE AND MAGNESIUM BISMUTHIDE
AS THERMOCOUPLE MATERIALS FOR THERMOELECTRIC POWER GENERATION

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SUMMARY

The principal goals of this program were to prepare pure, stoichiometric specimens of magnesium antimonide (Mg_3Sb_2) and magnesium bismuthide (Mg_3Bi_2) and to obtain information on their potential usefulness as materials for power generating thermocouples by measuring their Seebeck coefficients and electrical resistivities as functions of temperature.

Specimens of the desired quality were produced after much effort was put into perfecting the preparation process. The method finally adopted was fusion of the elements in a graphite crucible enclosed in a welded, argon-filled tantalum container; it was also necessary to purify the ingredients before use. Some trials were also made of zone-refining to purify the compounds and adjust their compositions. It was found that magnesium is an n-type doping agent in both compounds.

Electrical resistivities and Seebeck coefficients were measured up to 400°C on a sample of intrinsic Mg_3Sb_2 and up to 700°C on a sample of Mg_3Bi_2 at the end of the program. The results on Mg_3Sb_2 were not sufficient to determine the carrier mobilities, although it is clear that the techniques worked out during the program will be adequate to obtain this information in the future. The data on Mg_3Bi_2 suggest that it is a semiconductor up to about 200°C , is a semi-metal at higher temperatures, and may become a semiconductor again in the structure transformation which occurs at 700°C .

The room-temperature thermal conductivities of Mg_3Sb_2 and Mg_3Bi_2 were found to be 16 and 26 milliwatts/cm $^\circ\text{C}$ respectively by an absolute method, and an alloy of composition $\text{Mg}_3\text{Sb}_{0.4}\text{Bi}_{1.6}$ prepared late in the program was found to have a conductivity of 14 milliwatts/cm $^\circ\text{C}$. Thus the thermal conductivities of alloys of the two compounds must pass through a relative minimum lower than the conductivity of either pure material as the alloy composition is changed from one compound to the other.

Now that the preparation and measurement problems have been solved, further work should be done to make a final determination of the potential of these compounds and their alloys for thermoelectric applications. The fundamental properties of both compounds should be studied by more complete series of high-temperature measurements, and the dependence of the properties of the alloys on alloy composition should be determined.

INTRODUCTION

The present report describes the results of a program of research on the preparation and properties of the intermetallic compounds magnesium antimonide (Mg_3Sb_2) and magnesium bismuthide (Mg_3Bi_2) conducted under NASA Contract No. NASw-1307 in 1965 and 1966. The objective of this work was to evaluate the potential of the compounds as materials for power generating thermocouples.

Under the sponsorship of the U. S. Navy Bureau of Ships, the Advanced Technology Laboratories* of the General Electric Company had already put about two professional man years research effort into studies of Mg_3Sb_2 and Mg_3Bi_2 when the present contract began. This early work was performed under U. S. Navy Contracts No. NObs 78403 (in 1960-61) and NObs 86854 (in 1962-63); it was mostly concerned with the preparation of useful specimens of the materials, which proved to be exceedingly difficult. By the end of the latter contract it was felt that the preparation problems had been solved in principle; however, high-purity, stoichiometric specimens had not yet been obtained.

In the process of developing preparation methods, enough was learned about the fundamental properties of the compounds to provide incentive to continue research on them, and support for further work was sought from the National Aeronautics and Space Administration; this was obtained under Contract No. NASw-1307, which began September 27, 1965.

The program has been directed toward acquiring enough information about the fundamental electrical properties of Mg_3Sb_2 and Mg_3Bi_2 to permit a reasonable assessment of the properties potentially obtainable in heavily doped specimens. This was expected to be possible primarily because the partial information available in the literature about Mg_3Sb_2 was almost sufficient for this purpose, and only needed to be supplemented by accurate high-temperature Seebeck coefficient measurements on specimens of intrinsic semiconductor quality.¹ Practically no information was available on Mg_3Bi_2 except what we had been able to determine from nonstoichiometric and rather impure specimens during the two previous contracts mentioned above. Work on this compound was included in the scope of the contract because it is the only known intermetallic compound having the same structure as Mg_3Sb_2 . It was felt that understanding of either would come more readily as a result of work on both, and for later thermoelectric applications it was obviously desirable to have data on the only material with which one could expect to alloy Mg_3Sb_2 .

The work of the program fell quite naturally into two phases, the first comprising the effort necessary to prepare pure, stoichiometric specimens, and the second consisting of making and interpreting measurements of their fundamental electrical properties. The text of this report is organized along the same lines, with the first two major sections dealing respectively with work which was done on specimen preparation and measurements of specimen properties. The conclusions drawn from the results and our recommendations based on them follow in two final sections.

* Now a part of the General Electric Research and Development Center.

SPECIMEN PREPARATION

A list of the batches of Mg_3Sb_2 , Mg_3Bi_2 , and alloys of the two compounds prepared during the program is given in Appendix A of this report, together with data on compositions and variations of the preparation technique. The following text, on the other hand, discusses our general findings on the preparation and purification of these materials.

Summary of Chemical and Structural Properties

Magnesium forms a complete series of compounds of formula Mg_3X_2 with the nonmetallic elements of column V_A of the periodic table, and this series is divided into two classes with different structural properties. The compounds with nitrogen, phosphorous and arsenic have structures of the cubic Mn_2O_3 type (Strukturbericht type D5₃) with 80 atoms per unit cell. Magnesium antimonide and bismuthide, on the other hand, have the predominantly hexagonal La_2O_3 (Strukturbericht type D5₂) structure in their low temperature forms, with 5 atoms per unit cell.² Both Mg_3Sb_2 and Mg_3Bi_2 undergo a rapid, spontaneous structure transformation at high temperatures, accompanied by an easily detectable absorption of heat as the temperature is raised through the transformation point. Although structure determinations are not available, it has been suggested³ that both compounds transform to the Mn_2O_3 structure.

Mg_3Sb_2 and Mg_3Bi_2 are the only known intermetallic compounds having the La_2O_3 structure.⁴ Both have considerable solubility for excess magnesium in both the high and the low temperature modifications, but exhibit very little solubility for antimony or bismuth. It is likely that the large sizes of the Sb and Bi atoms are responsible for these compounds having the La_2O_3 structure instead of the more closely packed Mn_2O_3 structure. Numerical data on the structures of Mg_3Sb_2 and Mg_3Bi_2 are collected in Table 1, where it is interesting to note that the theoretical densities of the compounds are comparatively low although the molecular weights are large. This is a consequence of the open structure.

The significant temperatures in the constitution diagrams⁵ of the compounds are summarized in Table 2. In each compound, the maximum transformation temperature is found at the stoichiometric composition and the lower values indicated are for mixed crystals containing excess magnesium. The transformation temperatures of both compounds are above the maximum temperatures used in most thermoelectric power systems, and it may be noted that the Mg-rich eutectic temperatures are high enough so that the eutectic compositions could be used as cold junction joining alloys in thermocouple systems for most foreseeable applications.

Both compounds react with water or moist air. Mg_3Sb_2 apparently becomes covered by a protective surface film which limits the extent of the reaction. Mg_3Bi_2 evidently does not, for on prolonged exposure samples of the compound swell and eventually come apart along their layer planes. In their mechanical properties the two compounds are similar and about like metallic antimony.

TABLE 1

Structural Parameters of the Low Temperature
Phases of Magnesium Antimonide and Bismuthide

	Mg_3Sb_2	Mg_3Bi_2
Structure Type	La_2O_3	La_2O_3
Lattice Parameters		
a.	4.582 Å	4.675 Å
c.	7.244 Å	7.416 Å
Molecules per cm^3	7.5924×10^{21}	7.1242×10^{21}
Volume per Mole	79.3227 cm^3	84.5360 cm^3
Molecular Weight	316.436	490.896
Theoretical Density	3.9892 gm/cm^3	5.8069 gm/cm^3

TABLE 2

Melting, Transformation, and Eutectic Temperatures
for Magnesium Antimonide and Magnesium Bismuthide

	Mg_3Sb_2	Mg_3Bi_2
Melting Point	1228°C	823°C
Transformation Temperature	894-930°C	686-700°C
Mg-rich Eutectic	629°C	550°C
Eutectic	(10 at.% Sb)	(14.3 at.% Bi)
Sb/Bi-rich	579°C	260°C
	(86 at.% Sb)	(95.7 at.% Bi)

They have a Mohs hardness of 3 (Brinell hardness of about 7) and pieces dent before crushing in a mortar. A single large-grained polycrystalline sample of cast Mg_3Sb_2 has been tested by us in tension at room temperature; it exhibited an elastic modulus of 1.3×10^5 psi and fractures at a stress of 2490 psi.

Materials Used in Preparation

The antimony and bismuth used in this work were both of 99.999% purity, and were obtained from the American Smelting and Refining Company. This purity was considerably higher than that of the magnesium available from commercial sources, and both antimony and bismuth are almost completely inert to atmospheric gases. However, we considered it desirable to free both materials from the slight amounts of surface tarnish which were visible on the surfaces of the pieces as received.

This was done by melting and recasting both metals prior to use. The antimony or bismuth was placed in a quartz container with a small hole in its bottom, the container was mounted in a larger quartz tube connected to a high vacuum system, and heat was applied by an external furnace to melt the metal, which ran into a quartz cup below the container. Bismuth was melted in vacuum at about 10^{-6} Torr. Because antimony has a high vapor pressure at its melting point, it was melted under about one-half atmosphere pressure of pure argon. In each case a small residue of tarnished material remained in the melting vessel, while the castings were always bright and shiny.

It was more difficult to obtain magnesium metal of high purity. Inquiries from vendors advertising high-purity magnesium revealed that there are essentially two commercially available "pure" grades of the metal. One is primary electrolytic magnesium such as Dow Grade 5, which is of nominal 99.95% purity and contains manganese and iron as the principal impurities, as indicated by the spectrographic analysis given in Table 3. The other is redistilled magnesium analyzing about 99.98% pure, although one vendor claimed to be able to supply this material, at very high cost, in 99.996% purity. Another vendor indicated that his laboratory had zone-refined redistilled magnesium, but that the distribution coefficients of the impurities seemed to be unfavorable, since the refined product was not significantly more pure than the starting material.

Ordinary redistilled magnesium is produced as long, acicular crystals grown on the walls of carbon crucibles, and has a low bulk density because of large interstices occurring between the vapor-grown grains. This makes the material difficult to work with; primary electrolytic magnesium, on the other hand, is cast, free of voids, and can be cleaned easily. For the early preparations in this program, while the primary concern was to find ways of suppressing losses of magnesium from the batches, we therefore used electrolytic magnesium. When minor impurities came to be of concern, methods of cleaning the redistilled material and reducing it to solid form were developed.

The redistilled magnesium was freed of surface dross and the crucible fragments present in it as received through recasting by much the same method as that employed for the antimony. A melting crucible with a 1/8" diameter hole in its bottom and a mold to receive the molten metal were prepared from type AUC graphite. After the two graphite vessels had been baked out in vacuum, pieces of redistilled magnesium were melted in the crucible by induction heating under one-half atmosphere pressure of pure argon. In each case about half of the melt ran through the orifice into the receiving vessel, where it formed tapered castings entirely free of cold-shuts and other surface defects. Analyses of the starting material and cast product are listed in Table 3. We suspect that the increase in copper content after vacuum casting may have come from copper introduced into the graphite by machining, or possibly from the drill used to sample the cast material for analysis. In the latter case, of course, the increase would only be apparent.

TABLE 3

Spectrographic Analyses of Magnesium Metal from Various Sources

<u>Impurity Content, parts per million</u>			
<u>Impurity</u>	<u>Dow Grade 5 (Electrolytic)</u>	<u>As Received</u>	<u>Redistilled Vacuum Cast</u>
Mn	200		
Cu	20	< 10	20
Si	20	< 10	< 10
Sn	50		
Fe	1000	< 10	< 10
Al	20	100	100
Na	30	100	30
Li	0.5	< 10	< 10

Preparation Methods

All specimens of the compounds prepared during this program were synthesized by melting the elemental constituents together in vessels of high-purity graphite. Most of the difficulties encountered during the work had to do with the problems of protecting the batches and their containing vessels from atmospheric attack and preventing evaporation of magnesium during the high temperature heat treatments.

At the beginning of the program, we believed that it would be sufficient simply to enclose the batch and container in a sealed, evacuated stainless steel cylinder according to the method used by R. J. LaBotz for Mg_2Si - Mg_2Ge alloys⁶ and by this laboratory in previous work on Mg_3Sb_2 .⁷ It was realized that this preparation method entailed some losses of magnesium from the batch, but at first we attributed these mainly to absorption of Mg vapor by the graphite itself.

When this method of containment was used above 1150°C (which was necessary when preparing Mg_3Sb_2), it was necessary to keep the graphite vessel separated from the walls of the stainless steel container to prevent melting of the walls by formation of the carbon-iron eutectic. This was accomplished by setting rods of MgO in grooves in the walls of the graphite crucibles to serve as stand-offs. Occasionally, however, these separators would become displaced and a preparation run would fail. Another source of occasional failures was the pinchoff tube used to make the final closure of the stainless cylinder during preparations for a run; at high temperatures this became fragile and was easily cracked by any rough handling.

Finally, it was possible for the batches to become contaminated by manganese evaporated from the stainless steel unless special precautions were taken. Our method for avoiding this was to bake out the stainless steel parts under high vacuum (less than 10^{-5} Torr pressure) for three or four hours at 1100°C , to evaporate any manganese which could be removed from the surface. At this temperature the vapor pressure of manganese is about 1 Torr. Obviously, however, it was never possible to be sure that this process was completely effective.

In all, nine preparation runs were carried out by this method, using varying quantities of excess magnesium to make up for the expected losses. The results rather strongly suggested that it would not be possible to obtain intrinsic Mg_3Sb_2 or Mg_3Bi_2 by this means except by an unlikely coincidence. We therefore decided to explore improvements in preparation technique as well as methods of rectifying the compositions of the materials after synthesis.

A modification of the preparation technique eventually solved the problem. This change was based on a technique whereby H. Kroemer et al.⁸ had reported obtaining the compound Mg_2Ge with low carrier concentrations; it consisted of enclosing the graphite crucible in an evacuated tantalum container and then protecting the latter with an argon-filled outer jacket of stainless steel.

A photograph of the tantalum container design is shown in Figure 1. The container is made from .020" wall tantalum tubing, with a diameter of 1.5" and 6" length. Its ends are closed by welded tantalum plugs, one of which is provided with a 1/4" diameter tantalum pinchoff tube. It proved impractical to close off these tubes with a high vacuum inside, and they were therefore filled with high purity argon at one atmosphere pressure before running. The final closure of the container was made by pinching the tube twice and welding the end cut off by the second pinch. The pinchoff tube in this container was protected by the outer stainless steel jacket (made of Type 304L pipe with a 1/4" wall thickness) in which the container was enclosed. The stainless steel jacket in this assembly did not have a pinchoff tube; it was filled with argon by welding in end plugs of stainless steel in an argon-filled welding box.

To synthesize the compounds, the crucibles were laid on their sides in a laboratory muffle furnace and heated to temperatures about 50°C above the melting point of the compound in question. After being held for an hour at this temperature with intermittent agitation, each crucible was set upright in a vertical muffle furnace and cooled at a rate of 10°C per hour to a temperature well below the transformation temperature of the compound. The internal graphite vessels in these assemblies were provided with cylindrical specimen cavities in one end, so that the melted batch would form four rod-shaped castings 1/4" in diameter when the crucible was set upright. A typical cast batch with the four legs of the casting still attached to the cylindrical sprue is shown in Figure 2.

Nine preparations in all were carried out with this method, with only one failure, due to a malfunction of the temperature controller during the heating cycle. In this case the temperature evidently exceeded the tantalum-nickel eutectic temperature (1360°C), so that the wall of the tantalum container was

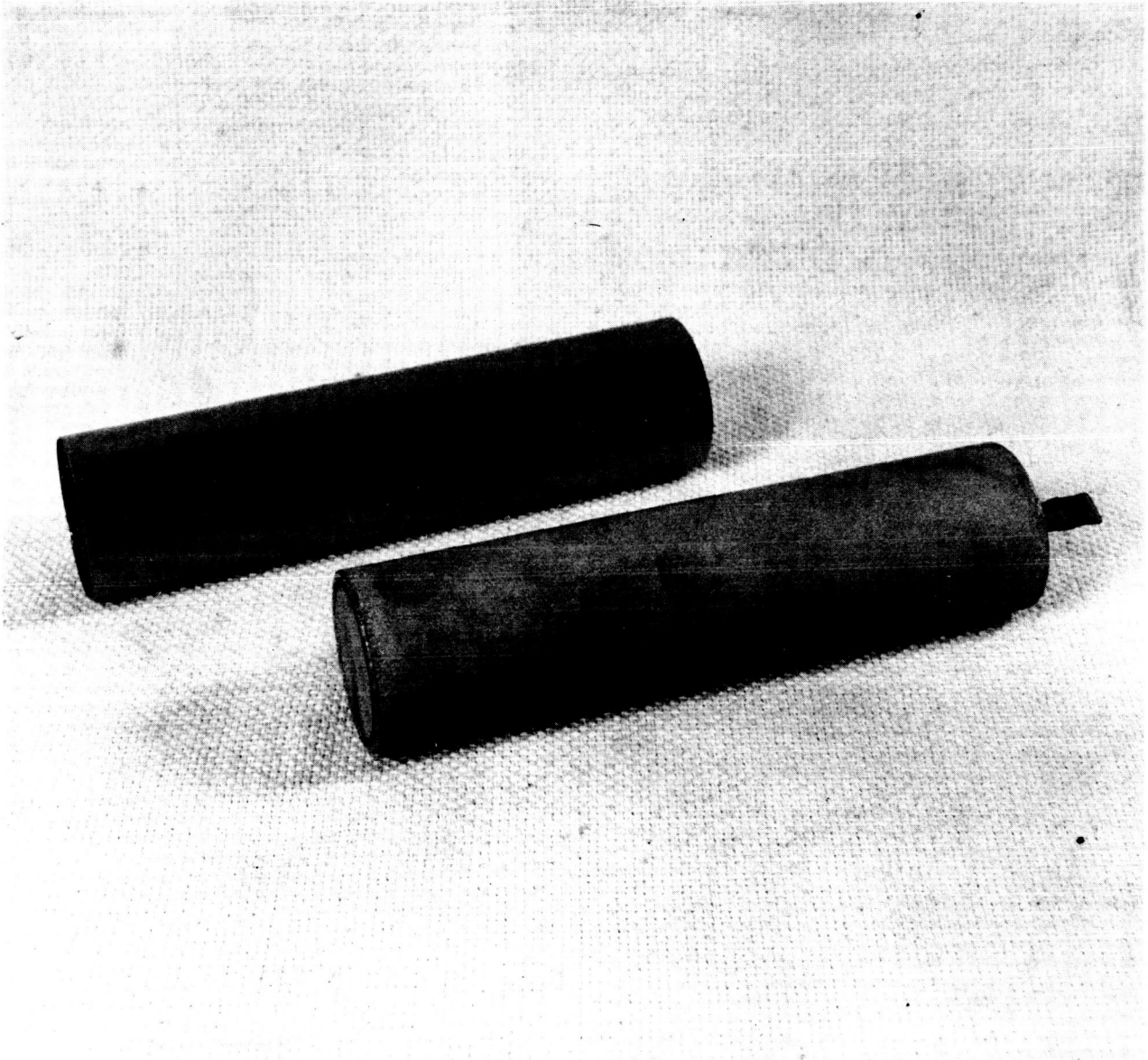


FIGURE 1 Two tantalum containers — Rear, before use; Front, after heating cycle. Note welded plug to left and pinched and welded tubulation at right. (R&DC Photo No. 1344).

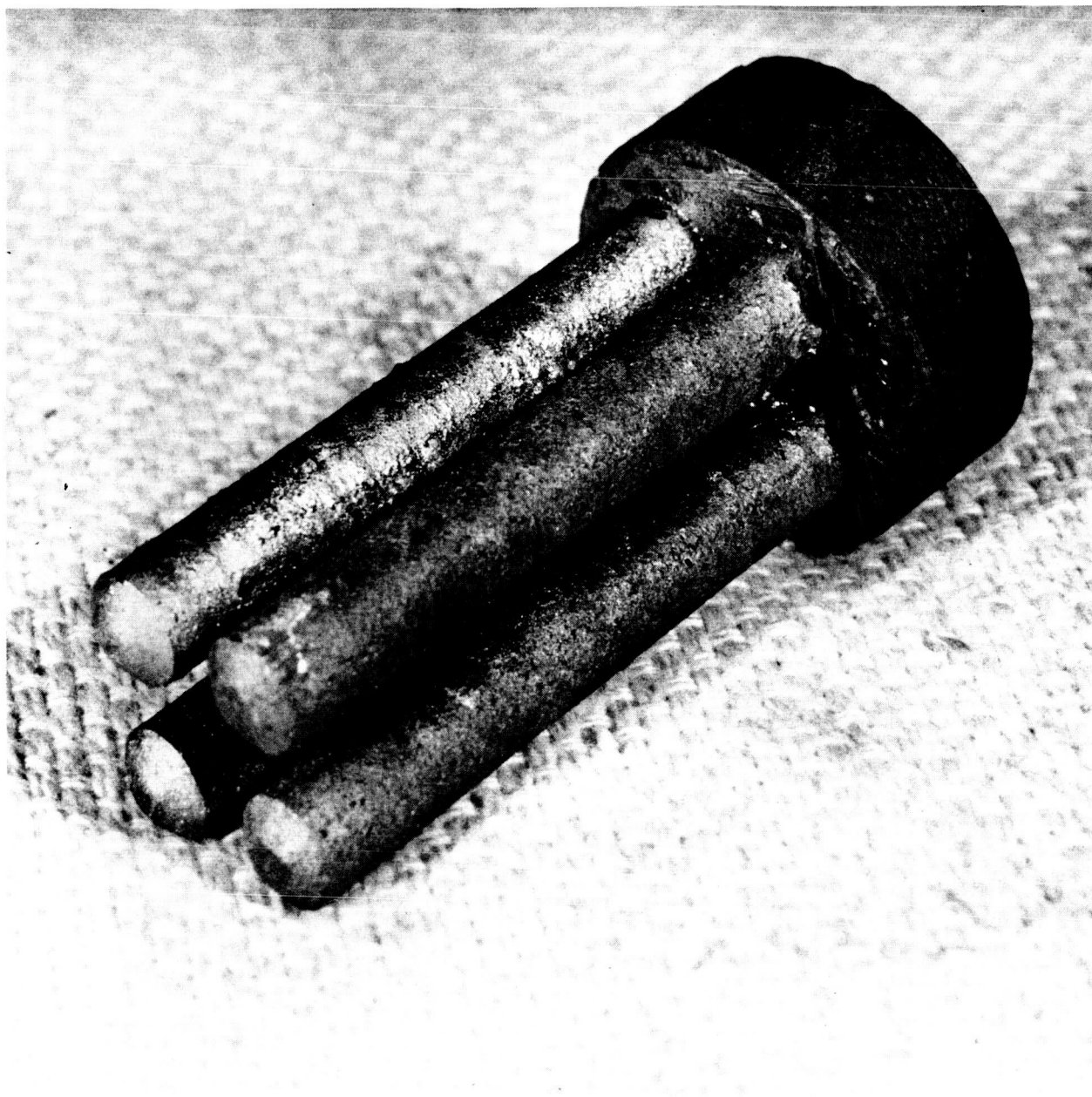


FIGURE 2 Typical batch of magnesium bismuthide as prepared, showing "four-legged" shape of ingot. (ATL Photo No. 885505).

pierced and the graphite crucible came in direct contact with the stainless steel. At all lower temperatures the tantalum was inert to the graphite and stainless steel; it had the further property of serving as an effective "getter" for residual air and water vapor in the argon atmosphere during the heating cycle.

The tantalum containers used in the later preparations were evidently quite effective in keeping impurity contents in the batches low. Table 4 shows the results of spectrographic analyses of samples from two batches (Batch M5051S-1 and M5051ST-2; see Appendix A) made to the formula $Mg_{3.05051}Sb_{2.00000}$ and synthesized respectively in an evacuated stainless steel container and in an argon-filled tantalum container. For comparison, the analysis of the Dow Grade 5 magnesium used to prepare both batches is also listed; it should be borne in mind that Mg_3Sb_2 contains only 23% Mg by weight, however, so that a given impurity concentration relative to magnesium is about four times as large as the concentration to be expected in Mg_3Sb_2 .

TABLE 4

Spectrographic Analyses of Two Batches of
 $Mg_{3.05051}Sb_{2.00000}$ and of Primary Electrolytic Magnesium

Impurity	<u>Content, parts per million</u>			
	Steel Container M5051S-1 (Leg 4)	Tantalum Container M5051ST-2 (Leg 1)		Magnesium Dow Grade 5
		#1	#2	
Mn	400	100	100	200
Cu	200	10	10	20
Si	80	10	10	20
Ca	80			
Pb	20			
Sn	20			50
Fe	10	20	10	1000
Al	10	10	10	20
Ni	10	20	20	
Ag	1			
Na	20	2	3	30
Li	< 0.5	< 0.5	< 0.5	0.5

It is fairly clear that the batches picked up manganese from the stainless steel containers, for the concentration shown in the first column of Table 4 is 8 times as great relative to magnesium as that found for the primary electrolytic grade Mg. It is possible, but less certain, that there was also some uptake from the tantalum. Tin and sodium appear to have been removed from the batch synthesized in the tantalum container, but more evidence would

be needed to confirm this. The concentration of iron was dramatically reduced below that present in the magnesium in both preparations, probably by reaction with the graphite crucible material.

It appears that the tantalum container material was substantially inert to the magnesium and antimony vapors evolved during the synthesis of magnesium antimonide, for batches prepared by this method had high resistivities and one had a resistivity of the order of 1000 ohm cm. Since the container was isothermal, with no cool spots where magnesium could condense, the amount taken up to fill the volume of the vessel with saturated vapor was negligible. It also appears that the type AUC graphite inner container did not absorb significant amounts of magnesium.

In fact, we believe that the principal factor controlling the stoichiometry of the preparations was the uncertainty in the weighing of the ingredients. An analytical balance and a set of calibrated weights were used to measure the amounts of magnesium, antimony, and bismuth used, and the quantities put into the crucibles were accurate to about ± 0.2 milligram in each 40-gram batch. The ratio of the number of magnesium atoms in a batch to the number of antimony or bismuth atoms was therefore $1.50000 \pm .00004$, and the number of atoms of one constituent in excess of the stoichiometric ratio could be as large as 10^{17} per cm^3 . Concentrations of this size are large enough to account completely for the observed variations in the electrical properties of the samples.

Zone Refining

When it became apparent that it might prove impossible to secure intrinsic specimens of Mg_3Sb_2 and Mg_3Bi_2 by empirical adjustment of batch compositions with the method of containment used originally in this program, we decided to try rectifying the compositions of prepared batches by zone-refining.

Zone-refining is a highly attractive semiconductor purification method in principle, because it is almost certain to produce a high-purity product eventually if it is properly performed. Moreover, it is an extremely effective method of removing low-melting minor phases due to the presence of excess constituents in intermetallic compounds; one passage through the material of a molten zone kept above the freezing temperature of the minor phase must remove all of it, unless some of the melt becomes trapped between grains of the freezing solid. On the other hand, ordinary zone-melting has the disadvantage that it yields that composition in a multicomponent system which has the highest melting point, and this may not be exactly stoichiometric. In the well-known cases of PbTe and SnTe , for example, the maximum melting point materials are heavily doped with excess tellurium. Also, zone-melting of an unfamiliar semiconductor material often requires extensive technique development before satisfactory refinement is obtained.

The arrangement used for zone-melting of Mg_3Sb_2 and Mg_3Bi_2 is shown schematically in Figure 3. The material to be refined was contained in graphite tubes because graphite was the only material obtainable in high purity and known to be inert to the molten compounds. The tubes were made from Type AUC graphite

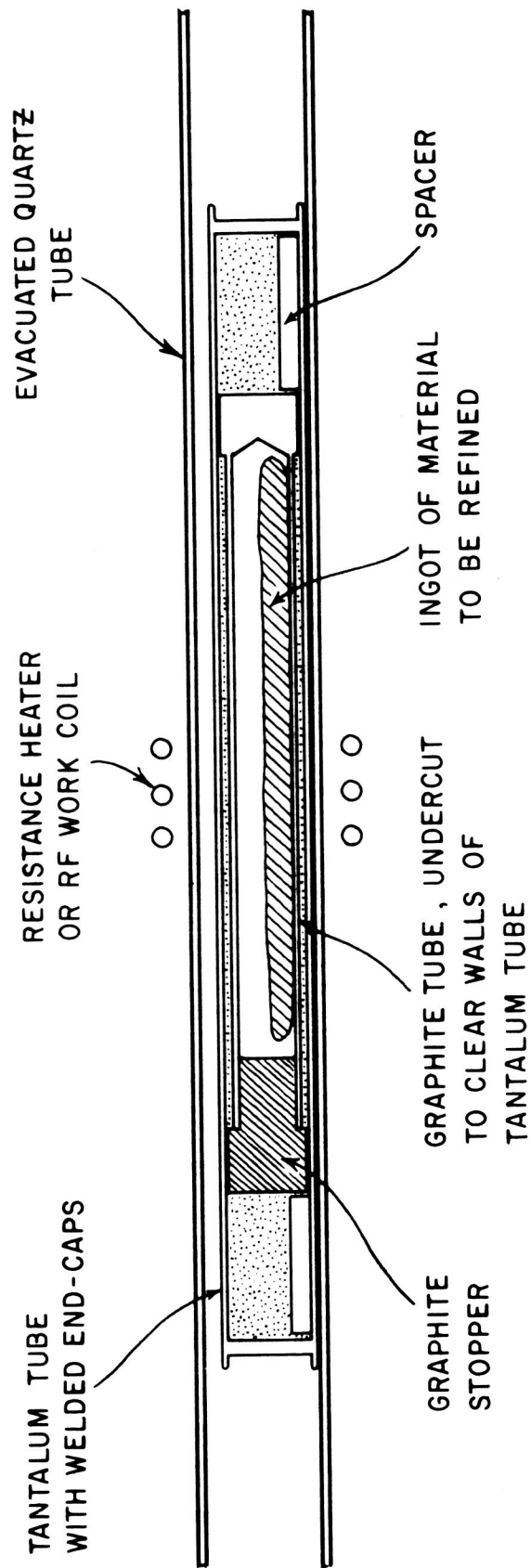


FIGURE 3 Zone-Melting Arrangement

and purified by baking out at 1500°C in a vacuum of less than 10^{-5} Torr. pressure. To minimize longitudinal heat conduction, their walls were made as thin as possible (about .03"). The tubes were closed by graphite stoppers made from the same material and similarly purified. To prevent losses of material by evaporation, the graphite tubes were enclosed in argon-filled tantalum tubes, closed with caps welded to the ends so that the entire capsule could be held at high temperature. The graphite tubes were kept centered in the tantalum capsules by spacers of MgO rod, as shown in Figure 3.

For the zone-melting runs, the tantalum capsule assembly was carried through a stationary RF induction heating work coil or resistance heating coil, in a quartz tube mounted on a movable carriage driven by a slow-motion motor drive. To protect the tantalum from oxidation, the quartz tube was evacuated. In order to prevent condensation of evaporated material anywhere in the tantalum capsule, a high ambient temperature was maintained around the assembly by two stationary tube furnaces (not shown in Figure 3) surrounding the quartz tube, one on either side of the zone heater.

The starting materials for the runs were 1/4" diameter rods cut from ingots like that shown in Figure 2. This made it necessary to do some preliminary melting of the material in order to draw it out into an elongated ingot like that sketched in Figure 3, a difficult process because the container was opaque and the ingot could not be seen.

In the first run with Mg_3Sb_2 , the preliminary melting process comprised a series of comparatively rapid passes of the end of the ingot into the RF induction heating coil. At each pass, more of the ingot length was run into the coil until on the last pass the entire length of the graphite tube was traversed by the high temperature zone. This procedure was probably effective in drawing out the ingot because the considerable expansion of the compound upon melting would have supplied a driving force to overcome the viscosity of the melt and push the free end of the ingot along the tube. At least the material was found distributed along the length of the tube at the end of the run. However, this first run failed because an excursion of the power input occurred on the fifth and last zone-melting pass, raising the zone temperature to about 1600°C. When the tube was opened it was found that the ingot contained two discontinuities, and we could not be certain of its state before the accidental overtemperature.

In the second run performed with Mg_3Sb_2 , the initial melting of the ingot was performed by enclosing the tantalum capsule assembly in an argon-filled stainless steel tube and heating it to 1280°C in a horizontal position in a muffle furnace. It was intended to make the melted material run out into the graphite tube by this procedure, but when the tube was opened at the end of the zone-refining run the ingot filled only about half of its length. We believe that it substantially retained its original shape during the preliminary melting, being held together while it was molten by the viscosity of the liquid.

The material used in this run was from the first batch successfully synthesized in a tantalum-jacketed crucible (Batch M5051ST-2; see Appendix A), and contained excess magnesium; the weights of Mg and Sb weighed out for the batch

were equivalent to the chemical formula $Mg_{3.05051}Sb_{2.00000}$. The zone-refining run comprised five passes of the molten zone through the ingot at a speed of 1.1 cm per hour, with a hot zone temperature of about 1250 to 1280°C and an ambient furnace temperature of 1000°C. The latter temperature was selected in order to keep the ingot above the structure transformation temperature (930°C) throughout the run.

Because of the failure to draw out the ingot to the full length of the graphite tube, the zone width, estimated to be about 1 cm, was about a third of the ingot length. The refinement attained in the five zone passes was therefore much lower than planned, but spectrographic analyses of opposite ends of the ingot indicated that apparently there had been some transport of impurities toward the last end to freeze, as shown in Table 5.

TABLE 5

Spectrographic Analyses of Ingot from Second Zone-Refining Run:
Leg #2 of $Mg_{3.05051}Sb_{2.00000}$ Batch Prepared in Tantalum-Jacketed Capsule

<u>Impurity</u>	<u>Content: parts per million by weight</u>	
	<u>First End to Freeze</u>	<u>Last End to Freeze</u>
Mn	40	50
Si	10	10
Fe	< 10	10
Cu	< 10	10
Li	< 1	< 1
Na	20	30

The material used in this run was from the same ingot that supplied the data for Table 4. Impurity levels are generally the same, except that manganese in this batch has the same concentration relative to magnesium as for Dow Grade 5 and nickel and aluminum are absent. The latter materials may have been removed by evaporation and reaction with the tantalum capsule, and it is possible that some manganese was also removed in this way. From the data it appears that manganese, iron, copper, and sodium tended to concentrate in the molten zone.

Seebeck coefficient measurements on this material were between +336 and +387 microvolts/°C before refining, and +315 to +369 microvolts/°C after; the resistivity changed from about 6 ohm cm before refining to about .05 ohm cm after. It seems quite unlikely that this large resistivity change was due to the slight redistribution of minor impurities depicted in Table 5; it more probably arose either from elimination of crystal imperfections or redistribution of an excess of one of the major constituents of the compound.

In the third and last run performed by this technique on Mg_3Sb_2 , no preliminary melting process was used. Instead the charge was made up of two 1/4" diameter rods from the first batch of stoichiometric material prepared in a tantalum-jacketed crucible (Batch No. M0000ST-1; see Appendix A); placed end-to-end, these rods filled substantially all of the space inside the graphite capsule.

Since there was little space between them, it was expected that the rods would merge during the first zone pass, and in fact this probably happened. Five zone passes were made at a speed of about one centimeter per hour with a zone temperature of 1250 to 1330°C as indicated by optical pyrometer measurements. When the tantalum tube was opened, it was found that the graphite inner capsule had ruptured, probably because of the volume increase of the charge on melting, and part of the material had flowed into the space between the tantalum and the graphite. As prepared, the material used in this run had given Seebeck coefficient measurements running from +256 to +559 microvolts/°C and resistivities from 2.3 to 6.1 ohm cm; after the run, measurements on the material remaining in the capsule gave Seebeck coefficients from +18 to +60 microvolts/°C and resistivities from 0.26 to 0.49 ohm cm.

The electrical measurements make it clear that the material was doped by the treatment it received, and it is reasonable to suppose that the doping was mainly produced by tantalum dissolved in the Mg_3Sb_2 . However, the tantalum did not appear to have reacted extensively with the charge when the assembly was inspected, and this visual impression was borne out by the results of a spectrographic analysis performed on the material remaining in the tube. These results are summarized in Table 6; the sensitivity of the measurement for tantalum was quite low, but with less than 1% tantalum by weight present it is unlikely that a new compound was formed.

All of the impurities detected by the spectrograph appear to have been moved toward the last end of the sample to freeze except for iron and titanium. Iron and titanium are known to be present in tantalum produced by the carbide-oxide process, however,⁹ and iron at least would be likely to be introduced in fabrication of the tubes used in the zone-refining apparatus.

The fourth run carried out with this apparatus was performed on Mg_3Bi_2 , using stoichiometric material synthesized in a tantalum-jacketed crucible with redistilled magnesium (Batch No. M0000BT-1; see Appendix A). In this case a single leg of the ingot was used to make the charge; it was split lengthwise and the two halves were laid end-to-end in the capsule. The run was conducted with a zone temperature of 870 to 900°C and an ambient temperature of 700°C (the structure transformation temperature) around the solid parts of the ingot. With this lower temperature, it was possible to use a loop of "Kanthal" resistance heating ribbon to maintain the molten zone instead of an induction heating coil. The resistance heater was easier to control so that it was possible to keep the zone temperature within narrower limits than with induction heating; with this arrangement it was also possible to run the apparatus unattended for long time periods, so that slower travel speeds were possible.

TABLE 6

Spectrographic Analyses of Ingot from Third Zone Refining Run:
 Legs #2 and #3 of $\text{Mg}_{3.00000}\text{Sb}_{2.00000}$ Batch
 Prepared in Tantalum-Jacketed Crucible
 (Batch No. M0000ST-1)

Content: parts per million by weight

Impurity	First End to Freeze	Center of Ingot	Last End to Freeze
Ta	n.d.* $< 10^4$	n.d. $< 10^4$	n.d. $< 10^4$
Si	200	100	50
Fe	20	10	300
Al	70	40	20
Cu	30	10	10
Ti	n.d.	200	n.d.
Sn	50	n.d.	n.d.
Pb	30	n.d.	n.d.
Ni	50	n.d.	n.d.

* "n.d." signifies that the impurity in question was not detected.

In this run five zone passes were made at a speed of 5 millimeters per hour, and the run was completed without incident. There was very little change in the electrical properties of the material, which had a Seebeck coefficient of +40 microvolts/ $^{\circ}\text{C}$ before and after the run and an average resistivity which changed from .40 to .52 milliohm cm. The results of spectrographic analyses performed on this sample after the run are given in Table 7, which again shows that the process is effective but that only small amounts of refinement were obtained in the number of passes made on the material.

The zone-refining run on Mg_3Bi_2 was so much easier than those attempted on Mg_3Sb_2 that we decided to try out a method for refining the latter compound at temperatures below 1000°C . The basis for this method was that the addition of an excess of either constituent to molten Mg_3Sb_2 or Mg_3Bi_2 lowers the freezing point of the melt, and the solid which is first formed at the lowered freezing point is Mg_3Sb_2 or Mg_3Bi_2 saturated with the dissolved excess constituent. Since the solubility of Sb in Mg_3Sb_2 or Bi in Mg_3Bi_2 is negligible, the solids which would freeze from Sb- or Bi-rich melts would be nearly stoichiometric Mg_3Sb_2 or Mg_3Bi_2 , and if the compounds proved to be doped by the dissolved Sb or Bi their compositions could be rectified by treatment with Mg vapor.

The method was especially attractive for Mg_3Sb_2 because there is a range of non-stoichiometric antimony-magnesium alloy compositions which are liquid at temperatures between the Sb- Mg_3Sb_2 eutectic temperature of 579°C and the Mg_3Sb_2 melting point at 1228°C . For example, an alloy containing equal numbers

TABLE 7

Spectrographic Analyses of Mg_3Bi_2 Ingot from Fourth Zone-Refining Run:
 Leg #1 of $\text{Mg}_3.00000\text{Bi}_{2.00000}$ Batch Prepared in Tantalum-Jacketed Crucible
 (Batch No. M0000BT-1)

Impurity	<u>Content: parts per million by weight</u>	
	First End to Freeze	Last End to Freeze
Fe	10	20
Al	10	20
Si	5	10
Ag	< 2	4

of Mg and Sb atoms becomes wholly molten at about 875°C . If liquid of this composition is in contact with solid Mg_3Sb_2 and the temperature is raised above 875°C , some Mg_3Sb_2 dissolves into the melt; if the temperature is lowered, some Mg_3Sb_2 freezes out. In either case, the composition of the liquid changes to new proportions which are in equilibrium with the compound at the new temperature.

In essence, the low-temperature zone-refining method attempted with Mg_3Sb_2 consisted of passing a molten zone with equal numbers of Mg and Sb atoms (so that its chemical formula would be MgSb) through an ingot of the pure compound. In an ideally executed zone-melting run, Mg_3Sb_2 would dissolve into the zone on its leading edge and freeze out on its trailing edge, leaving the composition of the zone invariant. With a slow enough speed of travel to insure that no liquid was trapped between crystal grains being formed at the advancing face of the freezing solid, the result would be to form an ingot of stoichiometric Mg_3Sb_2 , possibly with some antimony dissolved in it but without any eutectic precipitates.

The Sb-rich molten zone was to be produced by melting an appropriate quantity of Sb metal in contact with one end of a charge of stoichiometric Mg_3Sb_2 and dissolving enough of the compound in the melt to arrive at the proper zone composition. To apply the method successfully it was necessary to know the approximate volume of the molten zone produced by the apparatus so that enough antimony could be added to insure that the zone would be liquid at the selected temperature. It was also necessary to insure that the zone length would remain fairly constant through the run. On the other hand, it could be anticipated that a quite uniform product would be obtained if the zone remained molten, since the temperature dependence of the solubility of Sb in Mg_3Sb_2 is undoubtedly slight.

After one preliminary run had been conducted to establish operating procedures, a rod of Mg_3Sb_2 (Leg #3 from Batch M0000ST-1; see Appendix A) from a stoichiometric batch made in a tantalum-jacketed crucible was split lengthwise and the two halves were laid end-to-end in a graphite capsule as in the Mg_3Bi_2

zone-refining run described above. Previous measurements of the temperature profile along the length of the empty tube when it was stationary in the zone heater indicated that the zone should be about 1 cm long when the observed temperature was 900°C. Accordingly, enough elemental antimony was added to provide a 1:1 Mg:Sb ratio in a 1 cm length of the charge. The graphite tube was closed with a graphite stopper and placed in a quartz tube; the latter was then evacuated while its temperature was held at 150°C to drive off adsorbed water vapor and backfilled with argon gas to about one-half atmosphere pressure.

With furnaces on either side of the zone heater held at 600°C, the temperature of the zone heater was raised to about 900°C and the drive mechanism was actuated to move the graphite tube at a rate of 5 mm/hr. When the first passage of the tube through the heater was complete, the ingot was removed and inspected. It was found that the first half-inch of the charge had melted, but that the zone had not progressed through the ingot. This was interpreted to mean that the volume of material where the temperature was 875°C or higher was significantly longer than 1 cm, so that there was not enough antimony to produce a molten zone. Magnesium antimonide had evidently continued to dissolve in the zone until it had reached a composition whose melting point was above the zone temperature.

A second run was performed, with enough additional antimony added to allow for a zone length of 2 cm, but when this was completed it was found that only a little more of the ingot had melted. It had been expected that the temperature distribution along the tube would change when the ingot was placed inside, but the large change which evidently occurred was surprising. The results indicated that it would be necessary to modify the apparatus to produce a narrower zone before the scheme could be implemented successfully. By this time it had been found that Mg_3Sb_2 with high resistivity could be prepared by direct synthesis in the tantalum-jacketed crucibles, so the zone-refining activity was shelved. When it becomes necessary to produce material of higher purity than that of the available starting ingredients, however, we believe that this method of zone-refining will prove to be the most practical way of doing so.

Mg_3Sb_2 - Mg_3Bi_2 Alloys

In addition to the samples of Mg_3Sb_2 and Mg_3Bi_2 discussed above, one batch of an alloy of the two compounds was prepared during the program. This was done primarily to obtain preliminary information about their mutual solubility, but it was hoped also that data on its properties would indicate something of how the fundamental properties of the two compounds would combine.

The composition selected for the batch was 80 mol % Mg_3Bi_2 , 20 mol % Mg_3Sb_2 , so that the chemical formula of the alloy would be $\text{Mg}_3\text{Sb}_{0.4}\text{Bi}_{1.6}$. Since nothing was known of the melting point except that it was probably between those of the two compounds, the material was prepared by the procedure employed for Mg_3Sb_2 , using redistilled magnesium and a tantalum-jacketed crucible. In the first attempt to make the alloy the amount of magnesium was inadvertently made twice as large as it should have been, giving a batch which consisted of dendrites of the alloy embedded in a matrix of magnesium metal. Figure 4 shows the microstructure of this batch, which is typical of eutectic systems. The gray phase is the alloy and the white is magnesium; it is evident that the large

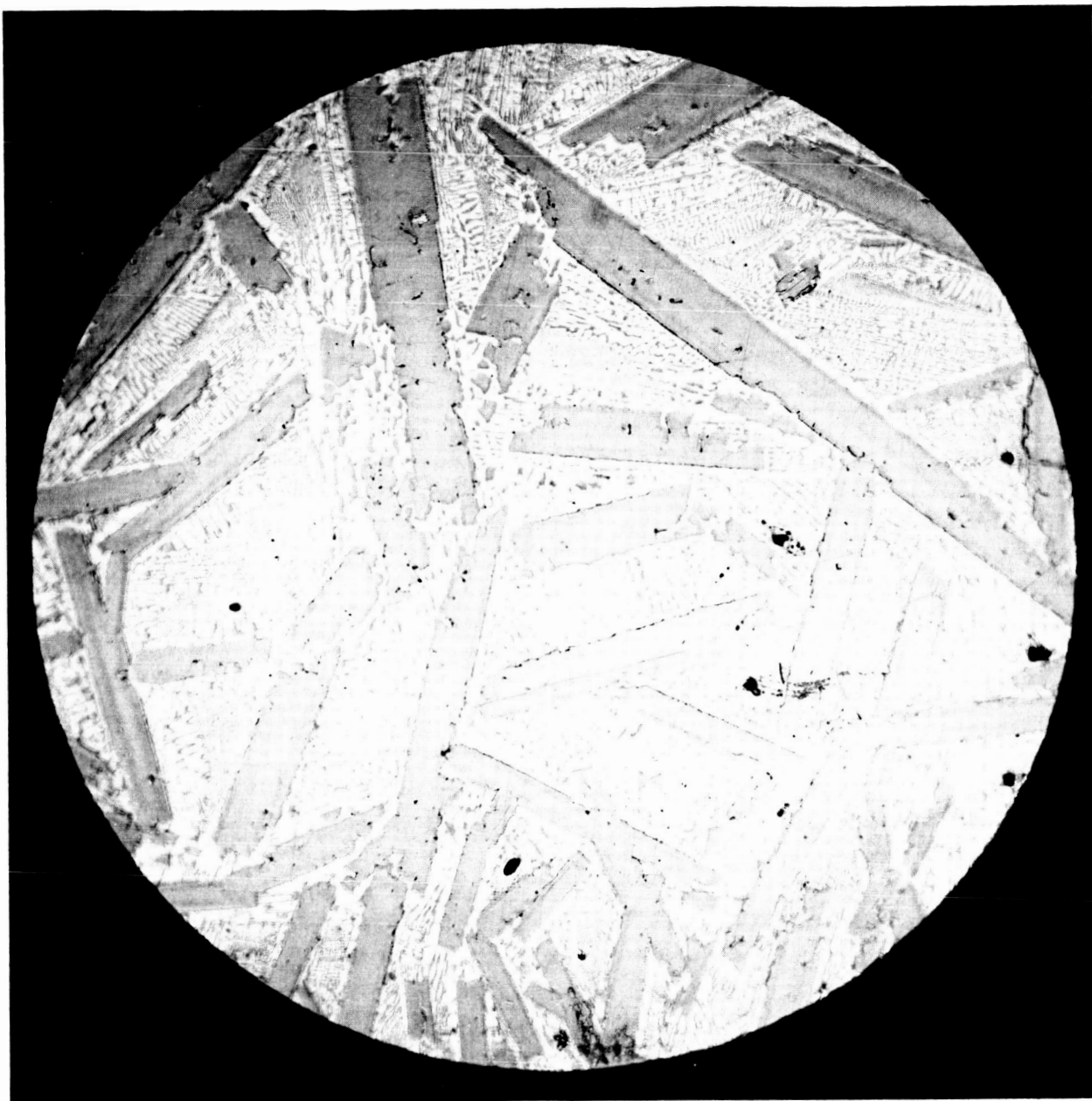


FIGURE 4 Microstructure of $\text{Mg}_3\text{Sb}_{0.2}\text{Bi}_{0.8}$ batch, showing dendrites of $\text{Mg}_3\text{Sb}_{0.4}\text{Bi}_{1.6}$ in magnesium metal matrix. Magnification = 25 X. (M&P Lab. Photo No. 6-4394C-1)

alloy crystals froze first, leaving a eutectic mixture of alloy and metal which froze at a lower temperature to form the intimate mixture of phases filling the spaces between the large grains. Within the alloy grains themselves, however, there was no evidence of coring or segregation; it therefore appeared that the two compounds were mutually soluble.

The latter conclusion was confirmed in our second, and successful, attempt to prepare an alloy of the same composition. The product proved to consist of a single metallurgical phase, similar in appearance to the compounds. Its properties are discussed in the following section.

PROPERTIES OF MAGNESIUM ANTIMONIDE AND MAGNESIUM BISMUTHIDE

Data Available in the Literature

In this section, by way of introduction to the description of the measurements made during the program, we summarize the data which were available at the beginning of the work and describe the reasoning which led us to expect that useful thermocouple materials might be developed out of Mg_3Sb_2 and Mg_3Bi_2 .

The most thorough previous study of the electrical properties of Mg_3Sb_2 has been that of Busch, Hulliger and Winkler.¹⁰ Their specimens were prepared by fusion of the elements in graphite under 10 atm. argon pressure¹¹ and they measured the Hall coefficient, Seebeck coefficient, and electrical conductivity over extended temperature ranges. In the intrinsic conduction range up to 1000°K the Hall and conductivity data accurately conformed to the following expressions:

$$\sigma = 9190 \exp(-4758/T) \text{ ohm}^{-1}\text{cm}^{-1} \quad (1)$$

$$RT^{3/2} = 65.6 \exp(4758/T) \text{ cm}^3 (\text{°K})^{3/2} / \text{coulomb} \quad (2)$$

$$R\sigma = 65.6 \left[\frac{T}{300} \right]^{-1.6} \text{ cm}^3 / \text{volt sec} \quad (3)$$

From these data, using well-known methods of interpretation¹², it is possible to draw the following conclusions about the band gap energy and carrier mobilities:

$$E_g(0^\circ\text{K}) = 0.82 \text{ ev} \quad (4)$$

$$\mu_p - \mu_n = 55.8 \left[\frac{T}{300} \right]^{-1.6} \text{ cm}^2 / \text{volt sec} \quad (5)$$

Since the difference between the carrier mobilities has very nearly the $T^{3/2}$ temperature dependence expected for carrier scattering by the longitudinal acoustic modes of lattice, vibration¹³, it is probable that this is the pre-dominant scattering mechanism.

The intrinsic conductivity at 300°K is about $1.2 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$, which at first sight does not seem promising. However, the coefficient in the formula (1) for the conductivity is large, and since the intrinsic carrier concentrations are apt to be quite small, it is possible that the carrier mobilities may also be large.

In normal semiconductors the band gap energy is temperature-dependent, following the expression

$$E_g = E_0 - \alpha kT \quad , \quad (6)$$

where α is commonly but not always a positive number between 3 and 4.¹⁴ If one substitutes this into the familiar formula for the intrinsic carrier concentration, the result is

$$n = p = 4.83 \times 10^{15} \left[\frac{m_n^* m_p^*}{m_0^2} \right]^{3/4} T^{3/2} \exp(\alpha/2) \exp(-E_0/2kT) \text{ cm}^{-3} \quad (7)$$

where m_n^*, m_p^* are the carrier effective masses and m_0 is the mass of a free electron. Substituting formula (7) into the formula for the conductivity

$$\sigma = ne\mu_n + pe\mu_p \quad , \quad (8)$$

and making use of the properties of Mg_3Sb_2 as expressed in equations (1) and (4), we find

$$7.73 \times 10^{-4} \left[\frac{m_n^* m_p^*}{m_0^2} \right]^{3/4} T^{3/2} \exp(\alpha/2) (\mu_n + \mu_p) = 9190 \text{ ohm}^{-1}\text{cm}^{-1}. \quad (9)$$

Thus at 300°K for example one has

$$\left[\frac{m_n^* m_p^*}{m_0^2} \right]^{3/4} \exp(\alpha/2) (\mu_n + \mu_p) = 2290 \text{ cm}^2/\text{volt sec}; \quad (10)$$

unless the effective masses are large and the band gap decreases very rapidly with temperature, the room temperature mobilities must both be large, for the difference between them is relatively small.

To get an estimate of the separate values of the mobilities one needs an independent measurement of some function of them other than those given by

equations (5) and (10). This can be supplied by the Seebeck coefficient, which is given by the following relation in an intrinsic semiconductor:¹⁵

$$S = \frac{k}{e} \left[\left(2 - \frac{\alpha}{2} + \frac{E_0}{2kT} \right) \frac{\mu_p - \mu_n}{\mu_p + \mu_n} - \frac{3}{4} \ln \left(\frac{m_n^*}{m_p^*} \right) \right], \quad (11)$$

where k is Boltzmann's constant (8.62×10^{-5} eV/°K). In an intrinsic semiconductor the numbers of free electrons and holes are equal, and if both types of carrier have the same mobility the Seebeck emf will be very small because the thermal diffusion currents down the temperature gradient will be equal and therefore cancel each other. The Seebeck emf will not entirely vanish, however, if the carrier effective masses are unequal, because the average carrier energies in the electron and hole currents will differ slightly.

Thus if one has Seebeck coefficient measurements on an intrinsic semiconductor over a reasonably wide temperature range it is possible to determine the value of the ratio $(\mu_p - \mu_n)/(\mu_p + \mu_n)$ by evaluating the derivative with respect to $1/T$. By combining the result with information such as that given by equation (5) one can then obtain values of the separate mobilities. By making use of the actual value of the Seebeck coefficient in conjunction with conductivity data such as equation (10) and employing the auxiliary relation¹⁶

$$m_p^*/m_n^* = (\mu_n/\mu_p)^{2/5} \quad (12)$$

one can also evaluate the effective masses and the temperature derivative of the band gap energy.

Busch et. al. attempted to carry out this program to evaluate the carrier mobilities and effective masses, but it is reasonable clear that the Seebeck coefficient data on which they relied were not adequate for the purpose. Only two samples were measured, and only one of these was approximately stoichiometric; the other contained 1% excess magnesium. The measurements on the nearly stoichiometric sample covered temperatures up to 750°K, and the Seebeck coefficient was positive over the whole temperature range. However, it exhibited a sharp relative maximum at about 475°K, so that the interval where it decreased generally as required by equation (11) with increasing temperature was only from 500° to 750°K. In this region the Seebeck coefficient decreased from 500 to 350 $\mu\text{V}/^\circ\text{C}$, with considerable scatter in the data. This scatter included an apparent relative maximum at about 650°K, and since the same feature appeared in the data on the sample containing 1% excess magnesium it seems probable that it was produced by something in the experimental technique rather than by the fundamental properties of the material. Moreover, the Hall mobility product $R\sigma$ for the nearly stoichiometric specimen deviated substantially from the intrinsic values given by equation (3) at all temperatures below 600°K.

In short, a close inspection of the data published by Busch et al. shows that the Hall mobility data on their nearly stoichiometric Seebeck coefficient specimen indicate deviations from intrinsic behavior over the temperature range where the Seebeck coefficient decreased approximately as $1/T$, and the Seebeck

coefficient data deviated substantially from the $1/T$ dependence expected of intrinsic material in the temperature range where the Hall mobility data satisfied the criteria for intrinsic behavior.

It was the intention of the program reported here to fill this gap in the available data on Mg_3Sb_2 by producing specimens with intrinsic electrical properties and measuring their Seebeck coefficients over a reasonably wide temperature range in which the $1/T$ dependence was satisfied. In addition, it was desired to develop preliminary information about the fundamental properties of Mg_3Bi_2 by preparing stoichiometric specimens and measuring their properties.

The basic factor which made the effort seem worthwhile was the possibility, discussed above, that Mg_3Sb_2 , or an alloy of that compound with Mg_3Bi_2 , might have high enough carrier mobilities at high temperatures so that one could dope the material to give a low resistivity over a wide temperature range, without having to introduce so many carriers that the Seebeck coefficient would have a low value due to degeneracy of the carrier distribution. It was expected that this question could be settled most rapidly and economically by determining the fundamental properties of the materials, rather than by an empirical study of the effects of various doping agents, because the fundamental approach could yield a general answer while the empirical approach could only show the effects of a selection of particular dopants.

Batch Evaluation Measurements

For much of the duration of this program the essential problem was to produce stoichiometric specimens of the compounds, with low enough carrier concentrations to permit measurements of the intrinsic electrical properties at moderately elevated temperatures. During this period we relied primarily on measurements of the densities, Seebeck coefficients, and electrical resistivities at room temperature to characterize the quality of the batches. The measured properties of the batches as prepared are summarized in Appendix A.

It was originally expected that accurate density measurements could be relied upon to detect excesses of the constituents in the samples, because in such cases the density of the product would deviate from the theoretical density determined from x-ray lattice parameter measurements. The density measurements were made by weighing the legs of the batches separately in methylene dibromide and in air, on an analytical balance in a constant-temperature laboratory, and correcting for minor variations in the liquid's density by comparison with a calibrated iron sample. On the basis of extensive series of measurements performed on lead telluride, we believe that the precision of this method is at least as good as $\pm 0.2\%$.

Since the compounds have negligible solubilities respectively for antimony and bismuth, it was expected that excess amounts of these constituents could be determined quantitatively on the assumption that any higher than theoretical density was due to the presence of a eutectic mixture of the compound and the excess component. In practice, the occurrence of small voids in the case samples limited the accuracy of the density determination; it can be seen in Appendix A that the densities measured on the four legs of a cast batch usually

covered a range larger than the estimated experimental uncertainty. However the accumulated data on the stoichiometric batches prepared late in the program all significantly exceed the theoretical densities obtained from literature values of the lattice parameters of the compounds. This strongly suggests that there are significant errors in the lattice parameters; in fact, the latter rest partly on density determinations evidently made on slightly non-stoichiometric samples, and the original authors¹⁷ concede that their values contain slight uncertainties. The discrepancies between the theoretical densities given in Table 1 and our data amount to about 1.2% and 1.7% for Mg_3Sb_2 and Mg_3Bi_2 respectively, and could be reconciled by adjusting the lattice parameters by amounts of the order of 0.5%.

Although scientifically interesting, this result was a disappointment because it meant that the density measurement could only be relied upon to indicate gross deviations from stoichiometry. Within the range of compositions encountered in this work, the electrical measurements furnished the only reliable guide to specimen quality.

The room temperature Seebeck coefficients of the batches were measured by resting the samples on a copper block, pressing a heated copper probe against the surface, and measuring the differences in temperature and electrical potential between the probe and block. This was done in a permanent apparatus which embodied certain refinements to insure that the measurements were made under conditions of thermal equilibrium and that the temperatures at the two contacts to the specimen surface were accurately determined. All of the room temperature measurements discussed in this report are given with respect to copper. Since the absolute thermoelectric power of copper is only + 1.88 $\mu\text{V}/^\circ\text{C}$ at room temperature, however, the values can be considered negligibly different from the absolute thermoelectric powers of the samples.

The instruments available for electrical resistance measurements were a Keithley Instruments Model 503 milliohmmeter with a four-point probe measuring head and a Dauphinee resistance bridge¹⁸ constructed in this laboratory. Resistivity measurements on the magnesium bismuthide and Mg_3Sb_2 - Mg_3Bi_2 alloy samples presented no problem with either instrument. However, magnesium antimonide forms a tenacious surface film with a very high electrical resistivity on exposure to even small concentrations of oxygen. For a time the limitations of the available instruments made measurements through point contact potential probes on Mg_3Sb_2 impossible because neither instrument had any sensitivity in the presence of the high contact resistances (of the order of 200,000 ohms) existing in the circuit. Resistivity determinations on all Mg_3Sb_2 batches through Batch No. M5051ST-2 (see Appendix A) were therefore made by simple d.c. methods, using knife-edge probes to obtain a relatively large contact area and measuring the potential drop with a Keithley Instruments Model 150AR micro-voltmeter, which had a very high input impedance. By the time the last (M0000ST-1, 2, and 3; see Appendix A) batches were prepared, however, a concurrent Company-supported program of apparatus development had provided an improved Dauphinee bridge circuit capable of working through very high lead resistances, and measurements on the three stoichiometric batches were made with this instrument.

It has been mentioned above that losses of magnesium by evaporation from the batches were expected to be the most serious problem in preparation, and that our original plan was to allow for these by adding suitable excesses of magnesium when the batches were weighed out. Accordingly, in the first half of the program the preparation and evaluation of batches were organized with a view to detecting excesses of the constituents in products obtained from initially magnesium-rich batches, and making empirical adjustments of the batch compositions to arrive at a stoichiometric product. All of the early batches were prepared with excesses of magnesium of the order of an atom per hundred molecules of the compound, and the high densities obtained for the Mg_3Sb_2 preparations lent credence to the supposition that the products were deficient in magnesium.

Various expedients were tried to reduce the losses which were believed to take place. Batch M5051S-2 was synthesized in a graphite crucible which had previously been heated to 900°C in a stainless steel bomb, with a charge of magnesium metal in the crucible instead of a batch of magnesium and antimony. The intention was to saturate the graphite with magnesium so that it could not absorb any from the batch when it was prepared afterward. Batch M5344B-1 was made in a graphite crucible which had been impregnated with graphite formed by pyrolytic decomposition of acetylene gas; here the idea was to fill the pores in the graphite and render it impervious to magnesium vapor. Batch M0000SD was a double batch, comprising two cylindrical castings of about 1" dia. \times 3/4" height prepared simultaneously in separate crucibles contained in a single stainless steel bomb. One ingot was made from a batch containing a considerable excess of magnesium (see Appendix A) and the other was made from a stoichiometric batch; it was hoped that the first batch would maintain a high enough magnesium vapor pressure to prevent significant losses from the second batch.

However, the density data on the early batches showed no systematic variation with the amount of excess magnesium, and the electrical properties of the materials were always approximately the same. Although the Seebeck coefficients varied considerably from one leg to another and from point to point on each single leg in the Mg_3Sb_2 batches, the values were always large and negative. In the successful Mg-rich Mg_3Sb_2 batches, the resistivities were always of the order of one to a few tenths of an ohm centimeter. Electrical properties measured on the Mg-rich Mg_3Bi_2 batches were more consistent, but again negative Seebeck coefficients were always obtained, except for one positive value found at a single point on one leg of Batch No. M5344B-1 (see Appendix A). Resistivities of these batches were generally between one-half and one milliohm centimeter.

On the other hand, the data available in the literature indicated unequivocally that intrinsic Mg_3Sb_2 has a positive Seebeck coefficient¹⁰ and it was expected that the properties of Mg_3Bi_2 should be analogous. Although the doping effects of excess constituents in the compounds were unknown at the beginning of the program, the accumulated results on the products of the Mg-rich batch preparations began to suggest strongly that the materials were doped n-type by excess magnesium.

This view was confirmed by the results of a series of experiments performed on the effects of various heat treatments on the properties of the magnesium-rich materials. The original intention of these experiments was to investigate the high-temperature stability of samples to be used for measurements of the

intrinsic electrical properties. Legs from the different ingots were placed in a quartz tube (coated with pyrolytic graphite on its inside surface to protect it from attack by the samples) and exposed for an hour at a time to various elevated temperatures. At the lower temperatures the tube was evacuated, since this was the easiest way to insure against attack by air and water vapor. At temperatures where sublimation began to be appreciable (700°C and above for Mg_3Sb_2 , 400°C and above for Mg_3Bi_2), argon gas at one atmosphere pressure was introduced into the tube to retard the sublimation and protect the samples. After each exposure the room-temperature electrical properties of the samples were measured.

It was found that exposures to temperatures as low as 200°C could reverse the Seebeck coefficients of both materials, and that stable p-type properties were obtained after exposures at 400°C. Because the work with the early samples had shown that the changes in properties were irreversible and generally did not depend on temperature above a certain threshold value, we adopted the practice of annealing all samples of the magnesium-rich materials at temperatures just below their respective structure transformations. The electrical properties measured before and after these anneals are summarized in Tables 8 and 9. In every case the Seebeck coefficient was reversed from n- to p-type; the resistivities of Mg_3Sb_2 samples were always substantially increased, while those of Mg_3Bi_2 samples were slightly decreased. The density changes associated with these treatments were always negligible.

On the other hand, when a sample from Batch No. M5051S-2 was heated at 700°C overnight (i.e., for about 16 hours) in a sealed vessel containing some magnesium metal, the result was only to increase the doping level slightly. This was indicated by the slightly smaller (but still negative) Seebeck coefficient and lower resistivity. Since the pressure of saturated magnesium vapor is at least 25 times as great as the magnesium vapor pressure in equilibrium with Mg_3Sb_2 ¹⁹ at 700°C, the sample could not have been deficient in magnesium after this exposure; in fact, it must have been saturated. When it was subsequently baked at 900°C, however, its properties fell within the overall range given for the batch in Table 8.

Thus there is little doubt that magnesium is an n-type doping agent in both Mg_3Sb_2 and Mg_3Bi_2 . When this was established, all further batches were prepared with stoichiometric proportions of the ingredients. As indicated in Appendix A, both stoichiometric Mg_3Bi_2 batches were p-type, while the three Mg_3Sb_2 batches exhibited the widely variable Seebeck coefficients and high resistivities characteristic of a wide-gap semiconductor with a small carrier concentration.

By the time these batches were prepared, the Dauphinee resistance bridge had been improved to such an extent that the resistivities of specimens of both compounds could be determined by the method of measuring their resistance profiles. In this technique a constant current is passed through the sample and successive measurements are made of the resistance of the material spanned between a fixed potential probe and one which is moved to a new position for each successive measurement. Thus the homogeneity of the sample can be determined in addition to its overall resistance.

TABLE 8

Effects of Heat Treatments on Electrical Properties of Samples
of Mg_3Sb_2 from Initially Magnesium-Rich Batches

Batch No.	Treatment	Room Temperature Electrical Properties
M3905S-3	As Prepared	$S = -226$ to $-358 \mu\text{v}/^\circ\text{C}$ $\rho = .049$ to $.125 \text{ ohm cm}$
"	Baked one hour at 900°C under one atmosphere argon pressure	$S = +127$ to $+597 \mu\text{v}/^\circ\text{C}$ $\rho = 4.8 \text{ ohm cm}$
M5051S-1	As Prepared	$S = -383$ to $-446 \mu\text{v}/^\circ\text{C}$ $\rho = .085$ to $.242 \text{ ohm cm}$
"	Baked one hour at 900°C under one atmosphere argon pressure	$S = +340$ to $+542 \mu\text{v}/^\circ\text{C}$ $\rho = 4.6$ to 9.6 ohm cm
M5051S-2	As Prepared	$S = -372$ to $-545 \mu\text{v}/^\circ\text{C}$ $\rho = .47$ to $.98 \text{ ohm cm}$
"	Baked overnight at 700°C in saturated magnesium vapor	$S = -295$ to $-430 \mu\text{v}/^\circ\text{C}$ $\rho = .242 \text{ ohm cm}$
"	Baked one hour at 900°C under one atmosphere argon pressure	$S = +251$ to $+495 \mu\text{v}/^\circ\text{C}$ $\rho = 1.5$ to 1.9 ohm cm
M5051ST-2	As Prepared	$S = -291$ to $-433 \mu\text{v}/^\circ\text{C}$ $\rho = .082$ to $.094 \text{ ohm cm}$
"	Baked one hour at 900°C under one atmosphere argon pressure	$S = +335$ to $+466 \mu\text{v}/^\circ\text{C}$ $\rho = 3.7$ to 14.3 ohm cm

The resistivities of some Mg_3Sb_2 samples varied by as much as 3:1 over the sample length, but samples with uniform resistivity also occurred. One of the latter had a resistivity of 1026 ohm cm, significantly higher than the expected intrinsic room-temperature resistivity of 833 ohm cm. Even higher values, up to 1545 ohm cm, were observed over major fractions of the less homogeneous samples. The properties of the stoichiometric magnesium bismuthide batches also presented some puzzles, for samples prepared by the method which evidently gave near-intrinsic Mg_3Sb_2 had lower resistivities than those which were obviously doped with excess magnesium. Moreover, although the occurrence of both positive and negative Seebeck coefficients makes it seem evident that the compound is a semiconductor, the absolute values are unexpectedly small and uniform. One would expect a semiconductor randomly doped by minor impurities or small excesses of the constituents to exhibit at least some Seebeck coefficient values greater than $\pm 200 \mu\text{v}/^\circ\text{C}$, the minimum positive and negative values

TABLE 9

Effects of Heat Treatments on Electrical Properties of Samples
of Mg_3Bi_2 from Initially Magnesium-Rich Batches

Batch No.	Treatment	Room Temperature
		Electrical Properties
M6714B-1	As Prepared	$S = -67 \text{ to } -93 \mu\text{V}/^\circ\text{C}$ $\rho = .645 \text{ to } .968 \times 10^{-3} \text{ ohm cm}$
"	Baked one hour at 650°C under one atmosphere argon pressure	$S = +41 \text{ to } +50 \mu\text{V}/^\circ\text{C}$ $\rho = .428 \text{ to } .690 \times 10^{-3} \text{ ohm cm}$
M3778B-1	As Prepared	$S = -61 \text{ to } -97 \mu\text{V}/^\circ\text{C}$ $\rho = .686 \text{ to } .844 \times 10^{-3} \text{ ohm cm}$
"	Baked one hour at 650°C under one atmosphere argon pressure	$S = +41 \text{ to } +52 \mu\text{V}/^\circ\text{C}$ $\rho = .306 \text{ to } .679 \times 10^{-3} \text{ ohm cm}$
M5344B-1	As Prepared	$S = +15 \text{ to } -91 \mu\text{V}/^\circ\text{C}$ $\rho = .694 \text{ to } 1.425 \times 10^{-3} \text{ ohm cm}$
"	Baked one hour at 650°C under one atmosphere argon pressure	$S = +41 \text{ to } +47 \mu\text{V}/^\circ\text{C}$ $\rho = .261 \text{ to } 1.125 \times 10^{-3} \text{ ohm cm}$

for semiconductors with a single carrier type and no degeneracy. Further discussion of these effects will be found among the conclusions at the end of this report.

Finally, as mentioned in the section on sample preparation, at the end of the program two attempts were made to prepare an alloy of 80 mol % Mg_3Bi_2 and 20 mol % Mg_3Sb_2 , of which the second was successful. Some measurements were made on the first batch before the mistake in proportions was discovered, but owing to the two-phase structure of the samples (see Figure 4) the measurements tended to give Seebeck coefficient values characteristic of the semiconductor alloy and resistivities characteristic of the magnesium metal matrix. When the true properties of the alloy were measured, both the Seebeck coefficient and resistivity turned out to be somewhat greater than the values for Mg_3Bi_2 prepared in the same way, and the density was reasonably close to the weighted average of the densities of Mg_3Sb_2 and Mg_3Bi_2 (5.45 gm/cm^3). The measured properties given in Appendix A, are about what one would expect if the variation of fundamental properties with alloy composition varied smoothly in passing from one pure compound to the other.

Mechanical Properties

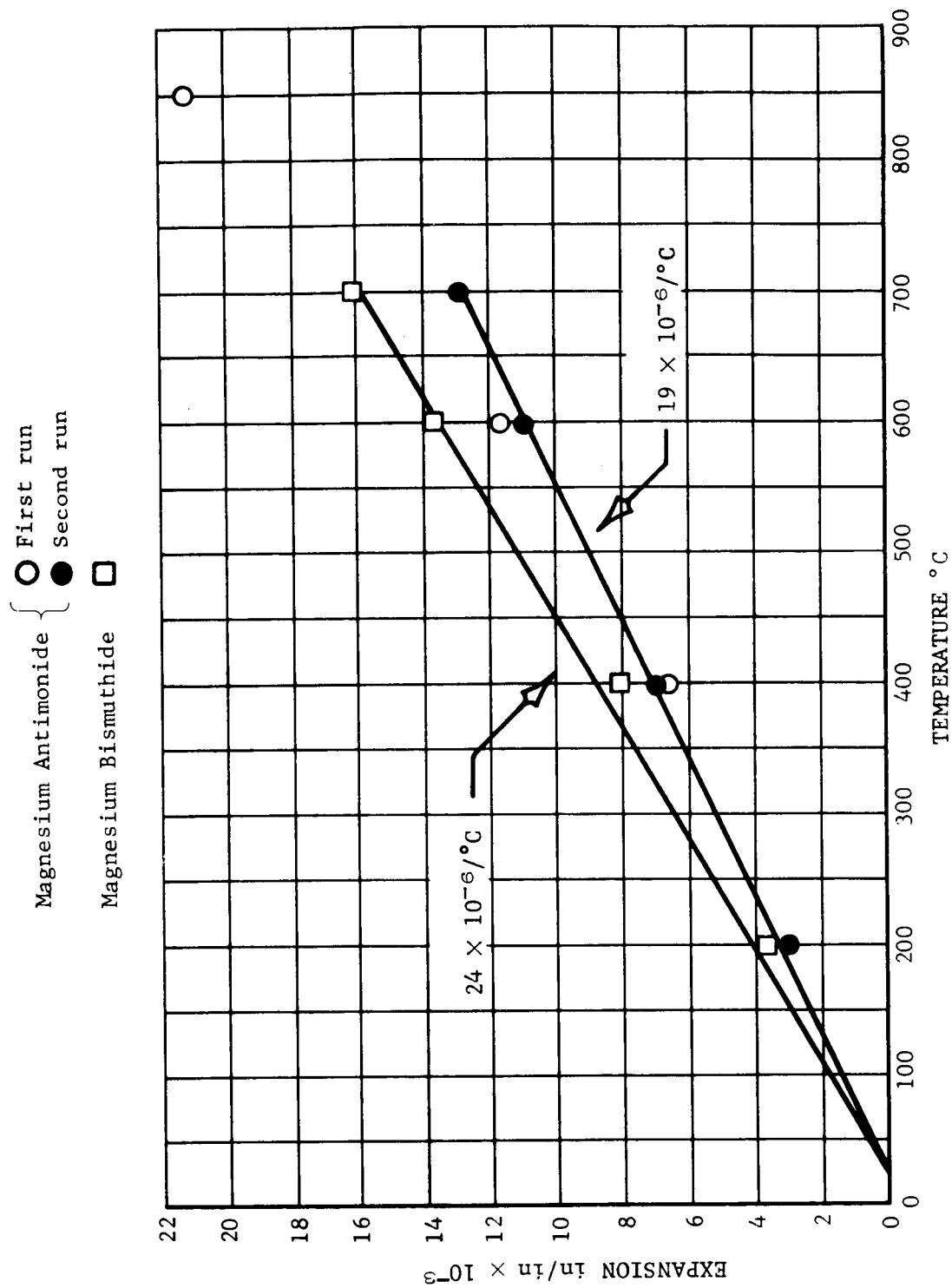
In the process of preparing samples and apparatus for various measurements, we accumulated a certain amount of information on the mechanical properties of Mg_3Sb_2 and Mg_3Bi_2 . Since the samples were all polycrystals with grain sizes of the order of a few millimeters, their observed properties are probably fairly representative of the mechanical behavior of single crystals.

As mentioned above in the discussion of the structural properties of the materials, magnesium antimonide and magnesium bismuthide are both soft and slightly malleable, with gross mechanical properties approximating those of metallic antimony. Both compounds have been successfully sawed, ground (both on paper and in a centerless grinding machine), drilled, and even tapped (using a jeweller's tap set in .012" to .028" holes). In tooling or machining these materials it was necessary to proceed cautiously and take light cuts to avoid cleavage fractures along the basal planes of the crystal lattice in the large grains. It was also necessary, of course, to prevent significant heating of the specimen surfaces and to avoid the use of coolants containing water.

In addition, certain effects arising out of the ductility of the materials were observed during machining. Polished surfaces on both compounds always had a burnished appearance, and it was found that fine drills (in the neighborhood of .010" dia.) were very apt to bind and break in the antimonide and the alloy material, although not in the bismuthide. It was also found necessary to use a toothed saw for cutting all of the materials rather than a diamond saw. When a toothed saw was used for cutting, the specimens could be held by simply attaching them to plates with wax; no special precautions had to be taken to support them from all sides. When diamond saws were used, cleavage fractures almost invariably resulted; we believe that this occurred because the diamond saws tended to drag the material with them, while toothed saws were able to cut out chips and carry them away without jamming them between the saw and the sides of the cut.

The thermal expansion coefficients of Mg_3Sb_2 and Mg_3Bi_2 were also measured to guide the design of jigs for measurements of the high-temperature electrical properties of the compounds. The measurements were made in a quartz dilatometer apparatus with a flowing argon atmosphere, and displacements due to the thermal expansion of the samples were measured with a linear variable differential transformer.

The data are plotted in Figure 5. It was hoped that the measurements could be carried up above the structure transformation temperatures of both compounds. However, it was found that the Mg_3Sb_2 sample became very soft at 850°C and began to deform under the spring pressure applied by the dilatometer soon after that temperature was reached. When a measurement was attempted at 750°C on Mg_3Bi_2 , the sample was lost because the temperature controller was mistakenly set at 850°C; however, the recorder trace obtained while the temperature was rising suggested that the sample became plastic as the Mg_3Sb_2 sample had done. It would be necessary to measure the expansion of the materials optically to get reliable data on either above about 700°C, and since optical apparatus was not readily available, we did not make the attempt.

FIGURE 5 Thermal Expansion of Mg_3Sb_2 and Mg_3Bi_2 

The straight lines plotted in Figure 5 are based on least-squares curve fits to the data obtained between room temperature and 700°C. The values of $19 \times 10^{-6}/^{\circ}\text{C}$ and $24 \times 10^{-6}/^{\circ}\text{C}$ obtained respectively for Mg_3Sb_2 and Mg_3Bi_2 are comparable to the value of $20 \times 10^{-6}/^{\circ}\text{C}$ which we have measured for PbTe . Since the thermal resistance and thermal expansion of a crystal lattice are both due to anharmonic components in the binding forces, the large and relatively constant expansion coefficients found for Mg_3Sb_2 and Mg_3Bi_2 probably indicate that the lattice thermal conductivities of the compounds decrease with increasing temperature as does that of PbTe .

We had originally intended to attach leads to the specimens for high temperature measurements by mechanically embedding them in the material. This seemed especially attractive in the case of the thermocouples to be used in the Seebeck coefficient measurements, because it would help to avoid temperature errors. Preliminary experiments on compatibility of various lead materials with the compounds had indicated that thermocouples sheathed in iron could be used. However, in view of the large thermal expansion coefficients of the materials, it seemed unlikely that we could rely on embedded leads to remain firmly in place, especially since it was to be expected that the electrical measurements would involve considerable amounts of thermal cycling.

High Temperature Measurements of Electrical Properties

Because of the larger than anticipated amounts of time and effort consumed in obtaining suitable specimens, only one sample each of Mg_3Sb_2 and Mg_3Bi_2 could be measured at high temperatures before the program ended. These measurements are described below. Although they were not complete enough to demonstrate whether the carrier mobilities in the compounds are large or small, they at least demonstrated feasible methods of measurement and developed preliminary information of some value. In particular, it was demonstrated that the high-resistivity Mg_3Sb_2 samples had intrinsic electrical properties near room temperature, and that the method of preparation therefore gave adequate control over the concentrations of impurities in the material.

The specimen holder used for high temperature Seebeck coefficient and electrical resistivity measurements on the compounds in this program is shown in Figure 6 with a specimen of Mg_3Sb_2 in place. The cylindrical sample, a piece cut from one of the 1/4" diameter legs of a batch, rested in V-shaped notches cut in two iron current electrodes held in a cylindrical Lava block at the bottom of the holder. Two parallel stainless steel tie rods were threaded into holes in this block and passed through clearance holes in a second, similar Lava block above the specimen. The upper Lava block was pressed down by a stainless steel weight which also ran freely along the tie rods, and two flat iron current electrodes mounted in the block were thereby held against the top surface of the sample. The dimensions were such that the current electrodes made contact with the specimen at three equally spaced points around its periphery near each end. Two pointed tungsten rods running through holes parallel to the axes of the upper Lava block and the weight (from which they were insulated by Lava spacers) were pressed against the upper surface of the sample by springs mounted in clamps attached to the tie rods at a point outside the picture area. The tungsten rods served as potential probes for a four-terminal resistivity measurement, and

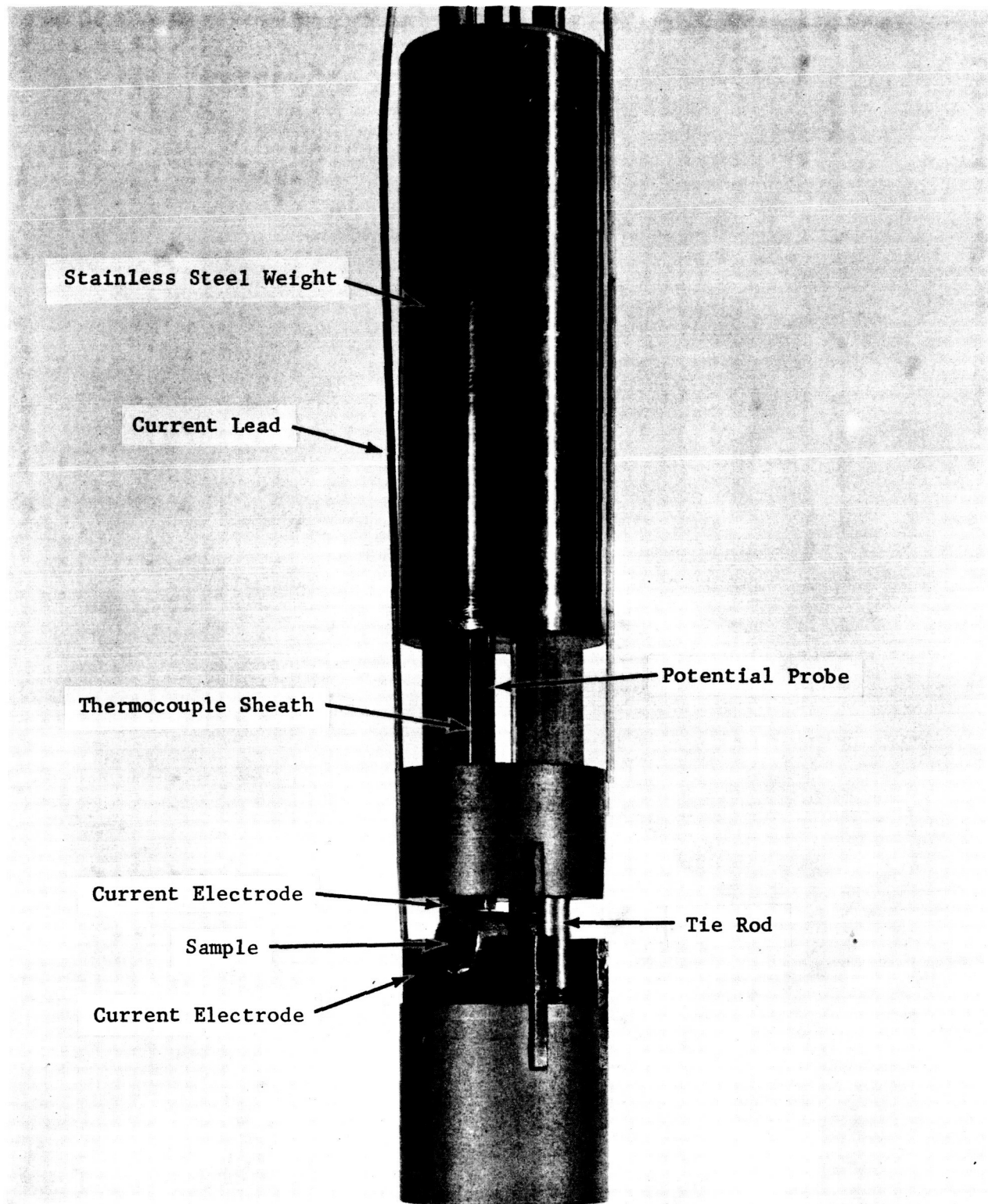


FIGURE 6 Specimen holder for high-temperature measurements of resistivity and Seebeck coefficient (R&DC Photo No. 7519)

spanned approximately the center third of the distance between the current electrodes. In this program the resistance of the material spanned by the potential probes was measured with the improved Dauphinee resistance bridge mentioned in the section on room-temperature measurements.

Temperature and potential measurements for the determination of Seebeck coefficients were both made through a pair of chromel-alumel thermocouples, each of which was sheathed in .030" o.d. stainless steel tubing. Each sheath was welded closed at the end containing the thermocouple junction, and the junctions were grounded to the sheaths at those points. Each thermocouple was pressed into a blind hole drilled in one of the upper current electrodes, so that the thermocouple junction was no more than .015" from the interface between electrode and sample. The stainless steel sheaths of the thermocouples were used as leads to carry current to the upper electrodes in the resistivity measurement, but could be isolated by opening their connections to the resistance bridge when Seebeck coefficient measurements were to be made. The temperatures of the two electrodes were measured by means of two Leeds & Northrup Type K-2 potentiometers connected to the thermocouples, and the Seebeck emf developed in the sample between the electrodes was measured simultaneously by a Hewlett-Packard Dymec Model 2401C integrating digital voltmeter connected between the chromel thermocouple leads. In all of the high-temperature data, the results were corrected to give absolute Seebeck coefficients by adding the absolute Seebeck coefficient of the chromel lead wire.

For protection against the atmosphere, the assembled jig was enclosed in a fused quartz tube, sealed off at its lower end and closed at its upper end by a brass header assembly with a quick-disconnect O-ring seal. Electrical leads were passed out of the enclosed space through a multiple-tube feedthrough in the top of the header assembly; the interior could be evacuated and backfilled through a vacuum valve permanently mounted to a sidearm on the header. An overall view of the quartz tube assembly, with the sample jig inside it, mounted in the furnace used to heat the apparatus is shown in Figure 7. The position of the jig in the tube was such that the sample was centered in the furnace, which was about 6" long; the thermal insulation wrapped around the tube above the furnace was intended to minimize heat losses by preventing gas convection around the outside of the tube and decreasing the temperature gradients in the parts of the apparatus inside.

The furnace itself was a "clamshell" type, consisting of two halves hinged together. The winding was therefore split in two, and in the setup shown in Figure 7 each half was powered by a separate autotransformer and controlled by a separate temperature controller. The white ceramic tubes carrying the temperature control thermocouples can be seen running along opposite sides of the quartz tube in the figure. Inside, the sample was oriented so that one end faced each half of the furnace; that is, so that the plane dividing the two halves of the furnace winding bisected the axis of the sample.

For resistivity measurements the sample was kept isothermal by running both halves of the furnace at the same temperature. When it was desired to produce a temperature difference between the ends of the sample to measure the Seebeck emf, the temperature of one half of the furnace winding was varied. This arrangement spared us considerable difficulties in the design of the sample

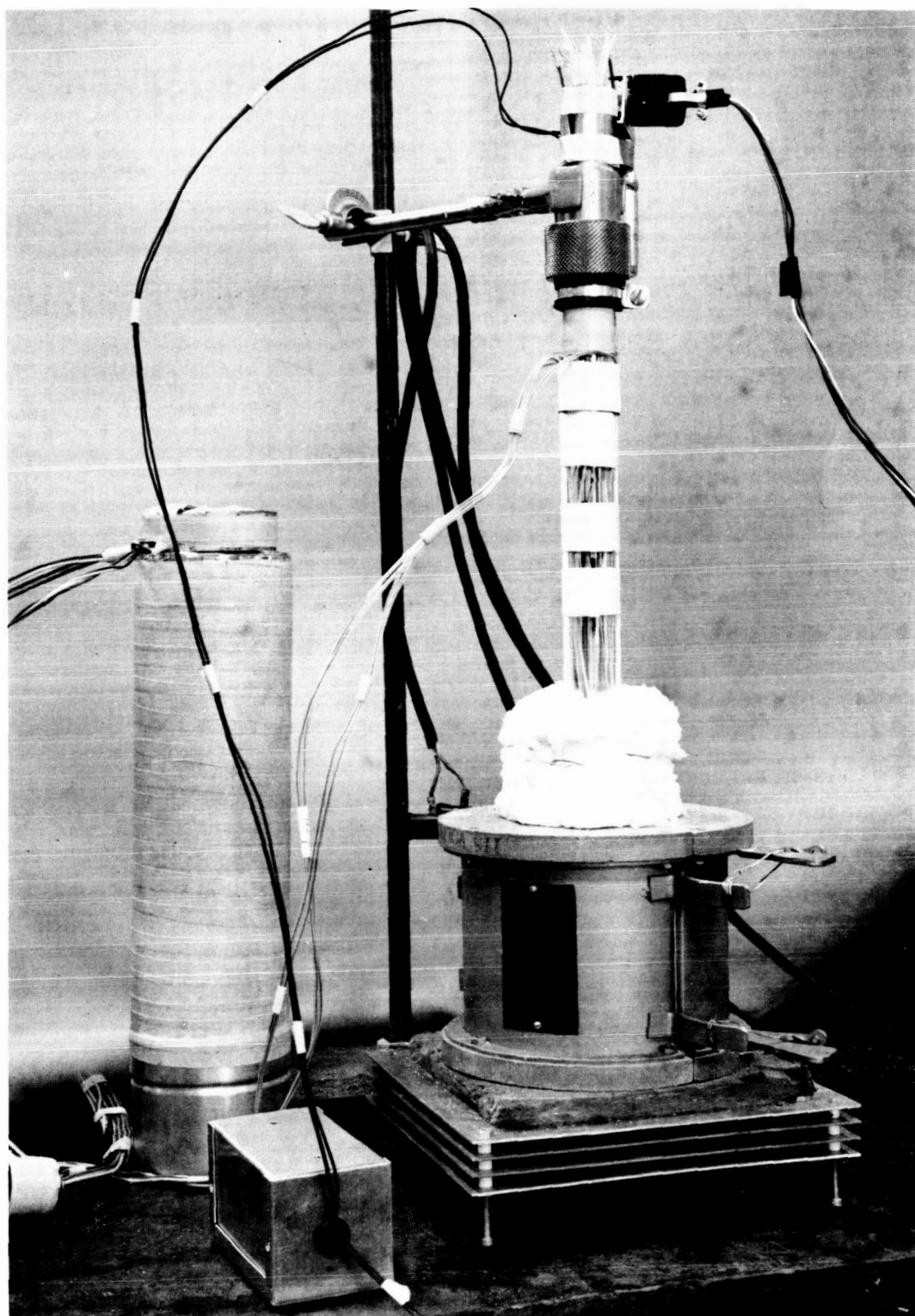


FIGURE 7 Overall view of sample enclosure and furnace setup for high-temperature electrical measurements (R&DC Photo No. 7517).

holder. To avoid uncertainties due to calibration errors in the thermocouples, the Seebeck emf was measured for a number of temperature differences between the electrodes at each average measurement temperature, and the Seebeck coefficient was calculated as the derivative of the Seebeck emf with respect to the indicated temperature difference.

All measurements were made either under a static vacuum or in a static argon atmosphere. Prior to a measurement run, the tube would be evacuated to a pressure at least as low as 2×10^{-6} Torr. and then backfilled if desired with high purity argon. As discussed below, however, it appears that the apparatus could not be depended upon to maintain an atmosphere of very high purity for more than about a day; in future work we plan to include a hot titanium wire "getter" in the arrangement to remove impurities from the gas.

The first measurements performed in this apparatus were made on a specimen from the most uniform leg of the Mg_3Sb_2 batch with the highest resistivity (Batch No. M0000ST-2; see Appendix A). The sequence of tests on this sample covered a period of ten days, but the quartz tube was evacuated and backfilled only once, at the beginning.

The resistivity and Seebeck coefficient data are plotted in Figures 8 and 9. When the sample was first heated, the temperature variation of the resistivity was in reasonably good agreement with the findings of Busch et al.¹⁰ as expressed by equation (1), up to 300°C. This can be seen in Figure 8, where the straight line representing the content of equation (1) has been plotted for comparison. Moreover, checks on the room temperature resistivity showed that it remained essentially unaltered after the measurements made at 300°C and below; this is indicated by the multiple room-temperature points clustered near 1000 ohm cm.

After the first measurement at 400°C, however, the room-temperature resistivity had fallen to only about 2 ohm cm. On repetition of the sequence it was found that the resistivity was substantially decreased at all temperatures below 400°C and that the room-temperature value was not significantly changed by reheating to 300°C. On the other hand, the first and second points taken at 400°C agreed quite well, and after the second 400°C measurement a further decrease was found in the room-temperature resistivity.

The Seebeck coefficient data shown in Figure 9 for the first heating cycle to 400°C reproduce those of Busch et al. on their nearly stoichiometric specimen, with the minor difference that in our data the relative maximum falls at a lower temperature and a higher Seebeck coefficient. This resulted from the lower carrier concentration in our sample; the one measured by Busch et. al. had a room temperature resistivity of only about 100 ohm cm.

The values of the Seebeck coefficient in the 0 to 300°C range were lowered by the process which decreased the resistivity in the first 400°C run, and were again lowered by the second cycle to 400°C. Evidently some sort of doping effect occurred, for according to the resistivity data the sample seems to have had a relatively constant carrier concentration up to about 100°C after the first run. On the other hand, the sample seems to have been intrinsic above about 300°C, as indicated by the virtual coincidence of the Seebeck coefficient values.

FIGURE 8 High-Temperature Resistivity Measurements
on Mg_3Sb_2 Sample (M0000ST-2; Leg #4)

- ⊙ Measurements taken during first heating cycle to 400°C
- Measurements taken during second heating cycle to 400°C
- ◇ Room temperature resistivity after second 300°C measurement
- △ Measurements taken after second heating cycle to 400°C

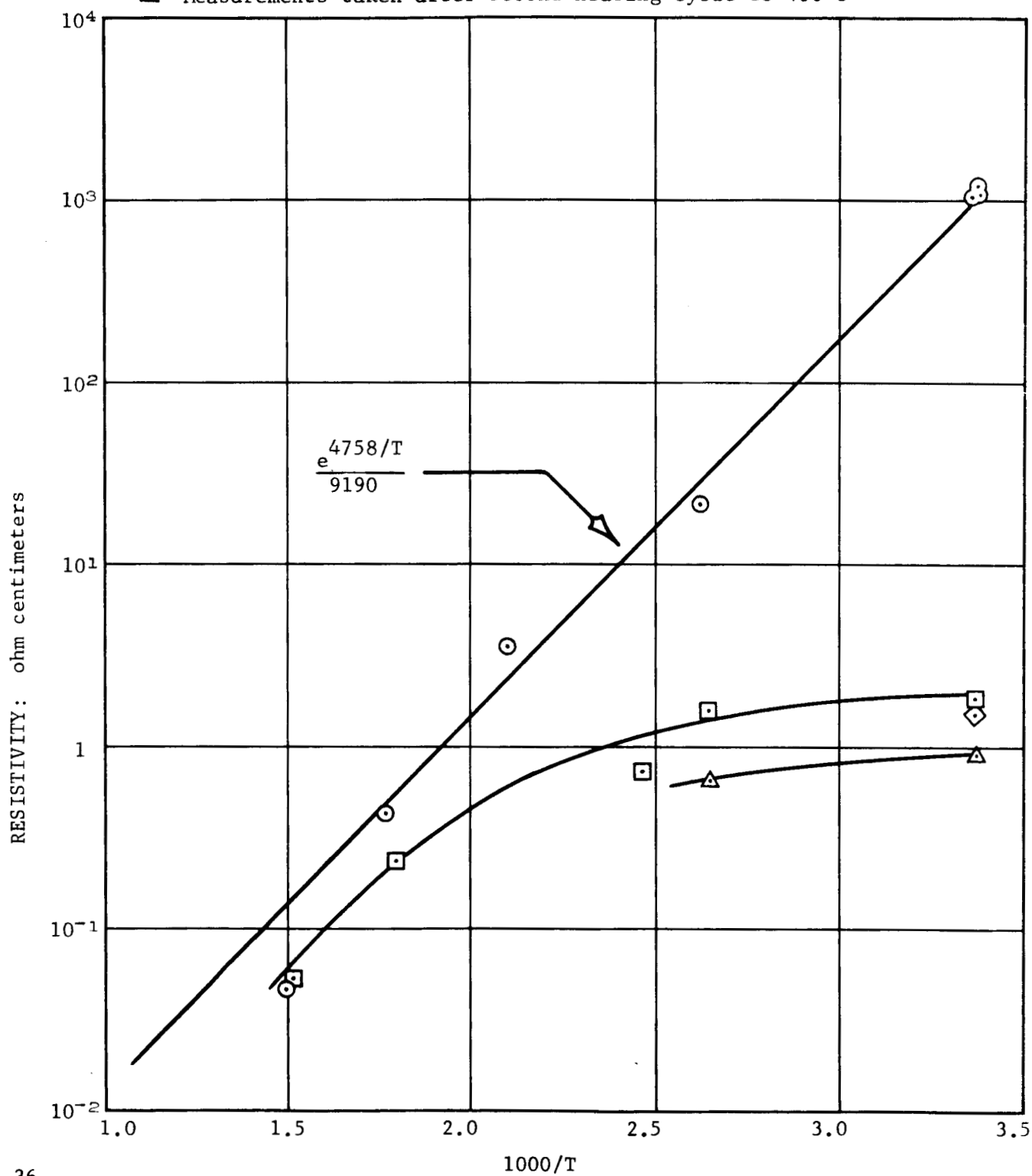
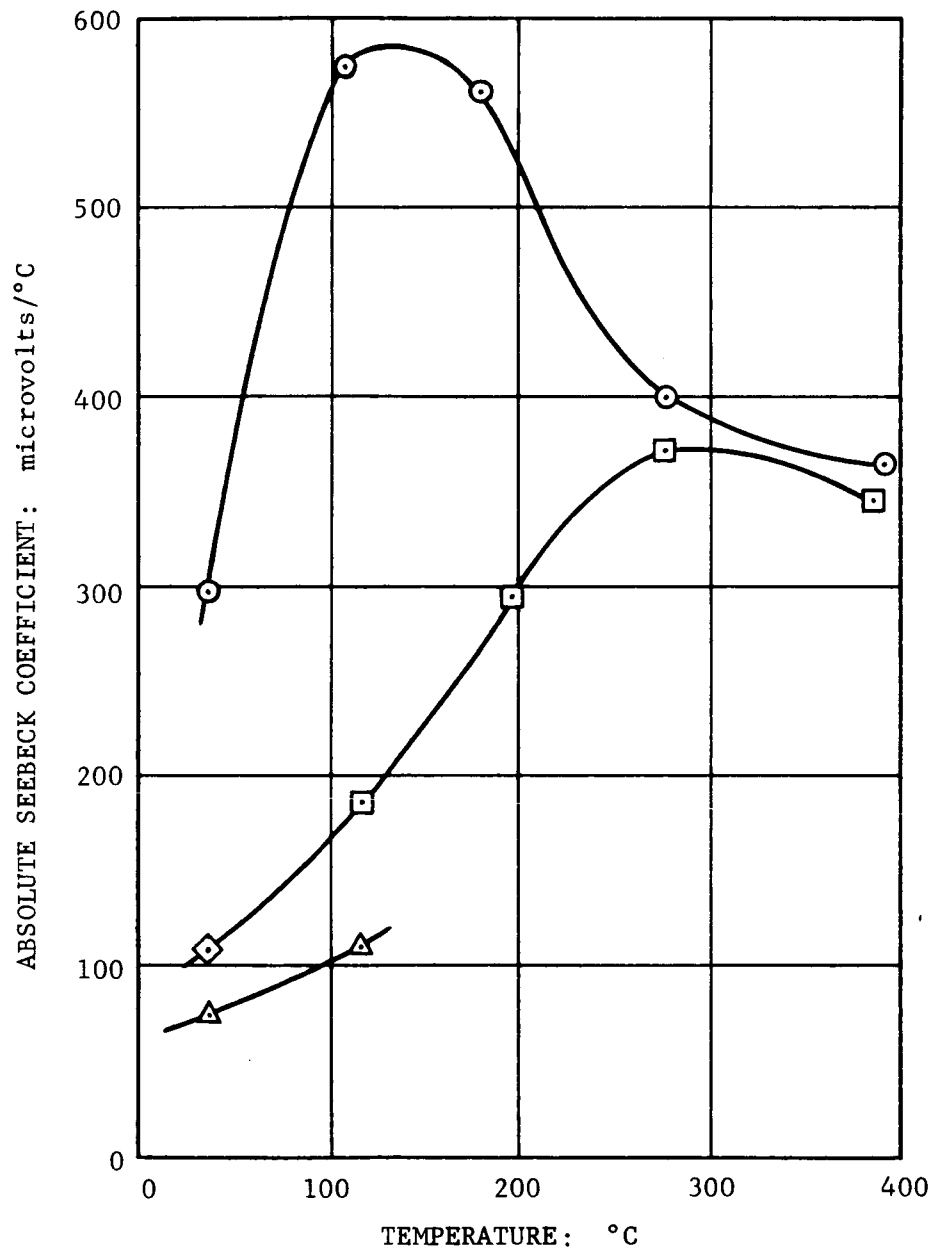


FIGURE 9 High-Temperature Seebeck Coefficient Measurements
on Mg_3Sb_2 Sample (M0000ST-2; Leg #4)

- ⊙ Measurements taken during first heating cycle to 400°C
- ▣ Measurements taken during second heating cycle to 400°C
- ◊ Room temperature value after second 300°C measurement
- △ Measurements taken after second heating cycle to 400°C



The data are insufficient to identify the nature of the doping effect, although we believe that it resulted from contamination of the atmosphere in the apparatus.

The results indicate that the high-resistivity Mg_3Sb_2 prepared by the methods developed in this program had intrinsic electrical properties near room temperature, and that it is certainly possible to obtain measurements of the intrinsic Seebeck coefficient over a wide enough temperature range to determine the mobility ratio. With reasonable caution, one could expect to obtain valid data over the temperature range from 300 to 800°C. The range in which the Seebeck coefficient had intrinsic values could be determined unambiguously by finding, from a reasonable accumulation of data, the temperatures at which the same values were obtained from specimens with slight doping differences.

A series of high-temperature measurements was also performed on one sample of Mg_3Bi_2 (from Batch No. M0000BT-2; see Appendix A). In these tests the apparatus was evacuated and backfilled with argon on the morning of each day when high-temperature measurements were to be performed, so that the time allowed for air to diffuse into the sample enclosure was never more than a few hours although the test sequence covered three weeks. Measurements between room temperature and 100°C were performed with the tube evacuated.

The data are given in Figures 10 and 11, and since there were no significant irreversible changes in the specimen properties, no attempt has been made to indicate the detailed thermal history of the specimen. The general procedure was to make measurements at successively increasing temperatures; each day's run also included a check of the room-temperature resistivity and a redetermination of the resistivity and Seebeck coefficient at some temperature where measurements had been made previously. Since the variations in the measurements obtained at any given temperature appeared to be random, we believe that most or all of the scatter in the data is due to experimental error. The resolution of the resistivity measurement was only a few tens of microhm centimeters because the signals obtained from the sample were near the sensitivity limits of the Dauphinee bridge circuit. The precision of the Seebeck coefficient measurement was of the order of a few microvolts per Centigrade degree, but occasional errors in executing the sequence of measurements and temperature changes could account for the larger deviations. The curve drawn in Figure 11 represents our estimate of which are the most reliable data points.

As we have mentioned above, it seems virtually certain that Mg_3Bi_2 is a semiconductor because we have obtained both p- and n-type samples. However, the resistivity of our sample increased with rising temperature rather in the manner of a semimetal, and the values of the Seebeck coefficient were so low as to suggest either a highly degenerate extrinsic carrier distribution or a distribution containing approximately equal numbers of electrons and holes with nearly equal mobilities. The latter idea is supported by our data on the several differently prepared batches, for although it was possible to reverse the sign of the Seebeck coefficient, the properties otherwise remained within a very narrow range of values.

There is a fairly definite suggestion of a relative minimum in the sample's resistivity between 0 and 200°C, despite the noise in the data in Figure 10, and between 200 and 600°C the resistivity increased approximately as $T^{3/2}$, as indicated

FIGURE 10 High-Temperature Resistivity Measurements on
Mg₃Bi₂ Sample (M0000BT-2; Leg #2)

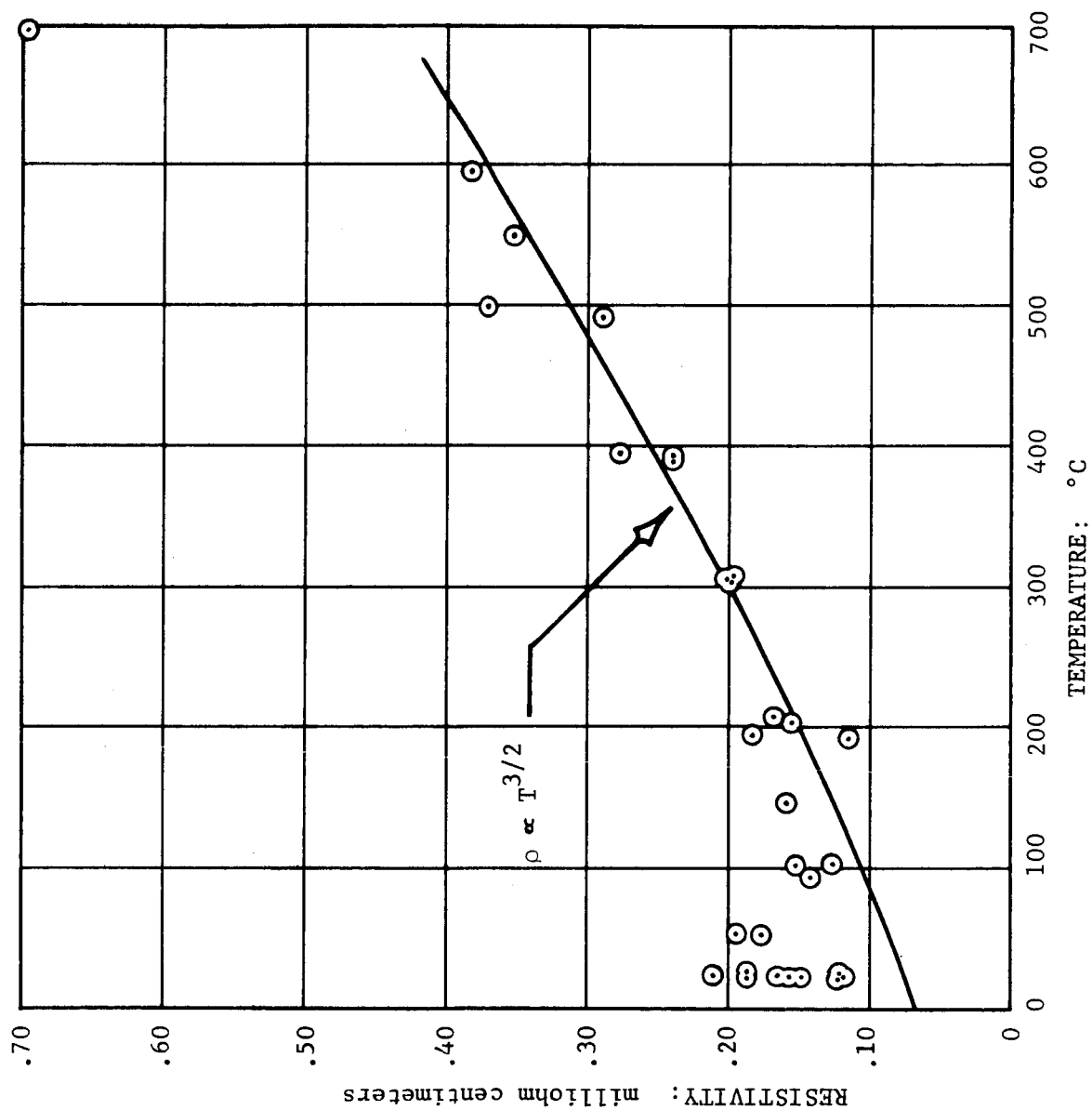
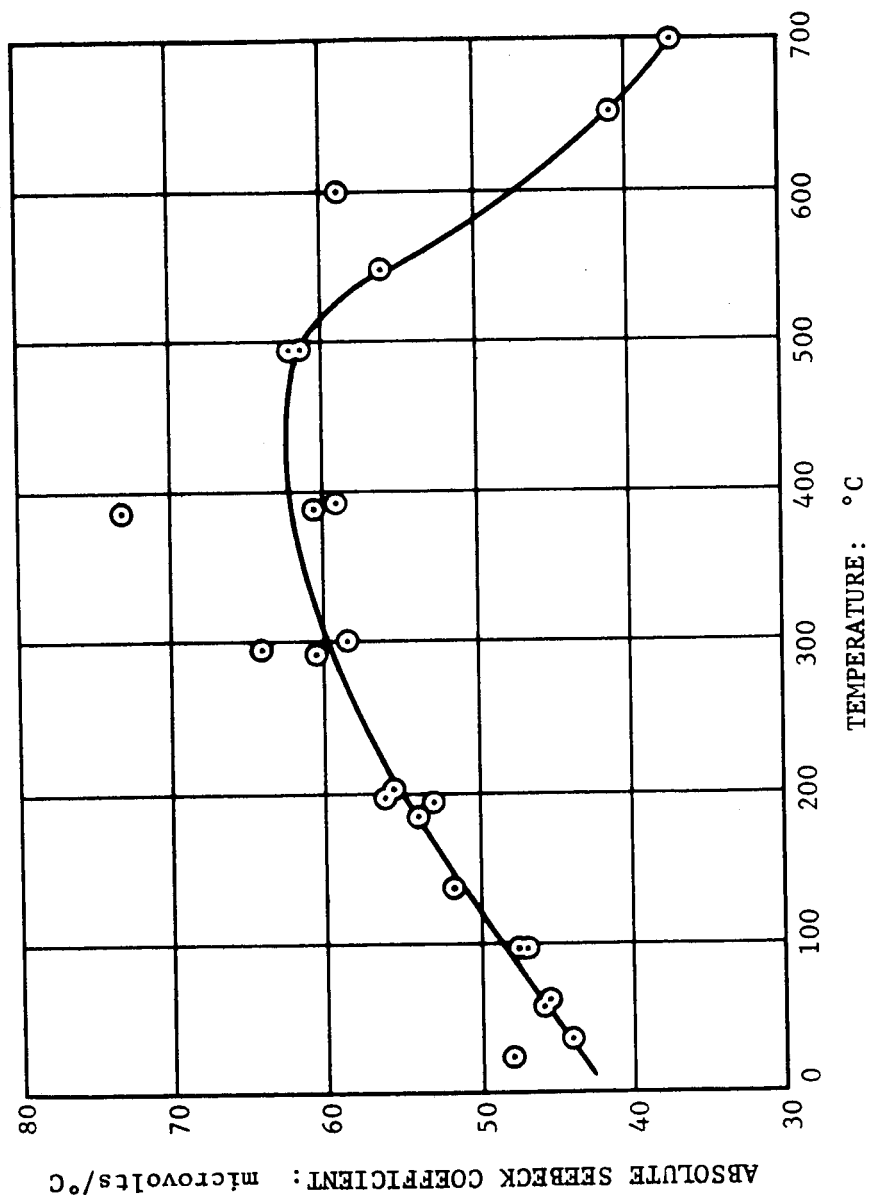


FIGURE 11 High-Temperature Seebeck Coefficient Measurements
on Mg_3Bi_2 Sample (M0000BT-2; Leg #2)



by the curve plotted for comparison in the figure. The single point obtained at 695°C may have been taken when the sample had already transformed to the high-temperature structure, for neither the original determination of the transformation point nor our temperature measurements during this sequence have enough precision to exclude the possibility. Obviously, no further discussion of the material's behavior near 700°C will be possible until more data have been accumulated; this particular sample was lost, however, when it melted during an attempt to secure a measurement substantially above the transformation temperature.

It appears probable that the extrinsic carrier concentrations in the stoichiometric Mg_3Bi_2 samples were no larger than those in the Mg_3Sb_2 samples prepared by the same methods from similar starting materials. We therefore believe that the behavior described above must result from special features of the Mg_3Bi_2 band structure rather than from doping. The apparent relative minimum in the resistivity may indicate that the compound is a semiconductor with a very small band gap at room temperature, but that the band edges begin to overlap at about 200°C. This interpretation would explain the apparent combination of semiconductive and semimetallic behavior. If it is a real effect, the rise in resistivity at the transformation temperature may come about because the volume expansion experienced in the transformation removes the overlap of the band edges and again converts the material to a semiconductor.

Such a transformation from semiconductor to semimetal and back again could make magnesium bismuthide an extremely interesting subject for study, particularly since the change at the structure transformation temperature must be quite abrupt. In our present state of knowledge, however, these ideas can be no more than speculations. More data are obviously needed; the measurements should extend downward in temperature at least to 100°K as well as upward to the melting point, and the sample geometry should be modified to increase the sensitivity of the resistivity measurement. Hall effect measurements should also be included in the data-taking scheme, since the changes in the character of these data with changes in doping can help to determine whether the behavior between 200 and 600°C is that of an extrinsic semiconductor or a semimetal.

Thermal Conductivity

Toward the end of the program, the completion of apparatus developed in another project made it possible to measure the room-temperature thermal conductivities of the materials by an absolute method, at little expense in time and effort. Since the values found in our previous work² were determined by the somewhat unreliable Powell comparator method²⁰, we considered it worth while to obtain more accurate data.

The essential features of the apparatus are illustrated in Figure 12. The sample was cemented to a copper heat sink with a silver-filled cement, and a small electric heater was similarly attached to its free end. Temperatures were measured at two points in the sample by small chromel-alumel thermocouples, sheathed in .010" o.d. stainless steel tubing and inserted in holes drilled radially so that the thermocouple junctions were located on the axis of the sample. This assembly was mounted on a brass base plate, through which the electrical leads were led by means of two ordinary octal tube bases. The sample

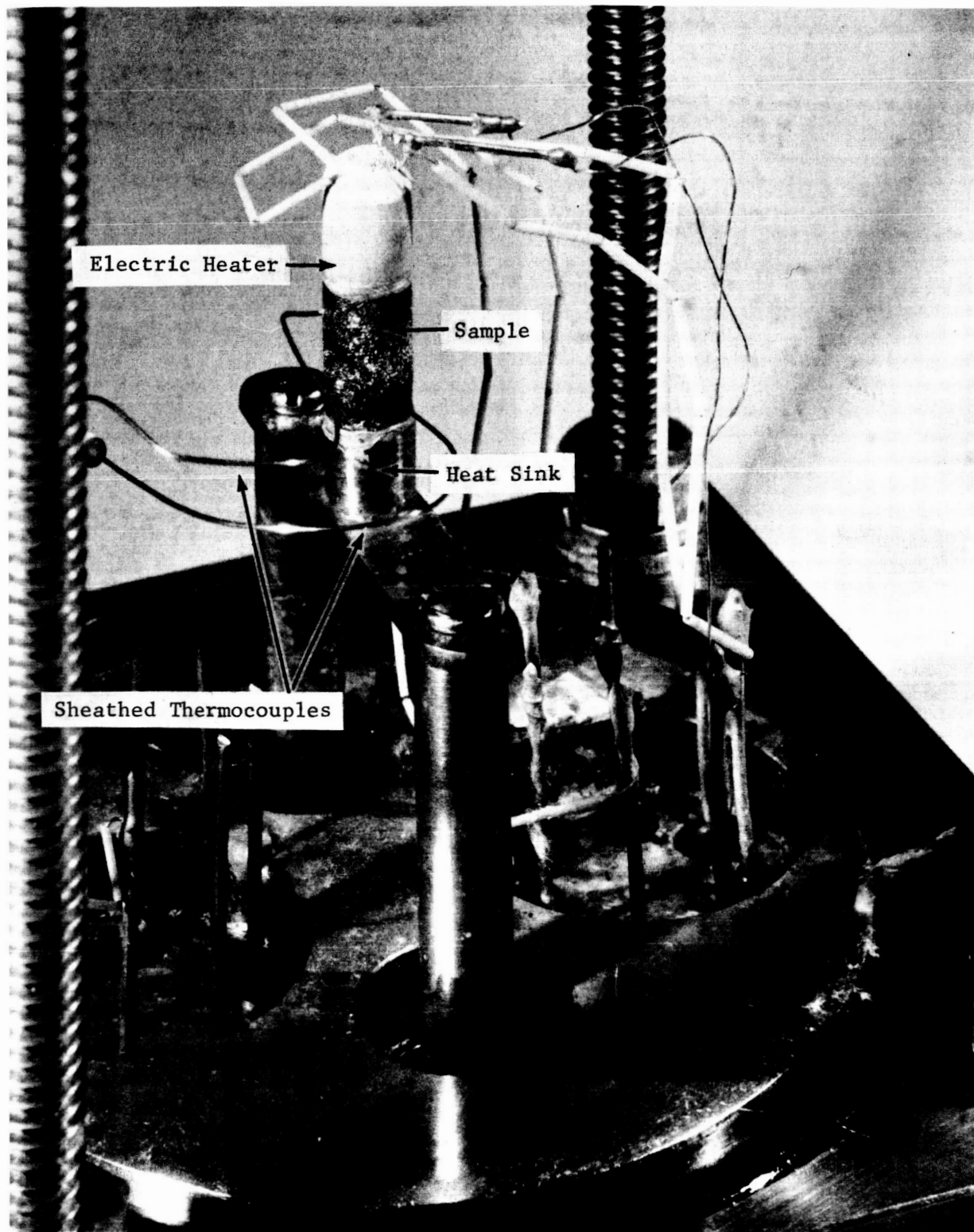


FIGURE 12 Sample mounted in room temperature thermal conductivity apparatus (R&DC Photo No. 7518)

assembly was contained in a vacuum-tight enclosure formed by a sleeve of brass tubing sealed to the base plate with an O-ring and a flat, O-ring sealed cover plate held on by the tie rods which are visible in the figure. The cover was provided with a valve through which the enclosure could be evacuated, and the sample was kept under vacuum at all times during measurements. The space around the sample assembly was filled with "Fiberfrax" thermal insulation to minimize heat losses.

In a preliminary series of runs, the heat losses from the heater through the thermal insulation to the heat sink and surroundings were calibrated by determining the amounts of power required to maintain the heater at various temperatures with no sample in place. Thermal conductivities were determined by mounting the samples as shown and measuring the temperature drop between the two thermocouple locations for two different values of heater input power. The previously calibrated heat losses were subtracted from the heater power to obtain the heat actually supplied to the sample, and this was divided by the measured temperature difference to calculate the thermal conductance between the thermocouple locations; the result was then multiplied by an appropriate geometrical factor to give the thermal conductivity.

The correction for heat losses ranged from 10 to 15% of the heater power, and from the reproducibility of the heat loss calibration as well as that of the measured thermal conductivity values found under different conditions, we estimate that the experimental uncertainties in our measurements are approximately $\pm 2\%$. Three samples were measured during the present program, with the results listed in Table 10.

TABLE 10

Room Temperature Thermal Conductivities of Samples of
 Mg_3Sb_2 , Mg_3Bi_2 , and an Alloy of the Two

Material	Specimen	Room Temperature Thermal Conductivity milliwatts/cm $^\circ\text{C}$
Mg_3Sb_2	M0000ST-2; Leg #1	16.4
Mg_3Bi_2	M0000BT-2; Leg #3	25.9
$\text{Mg}_3\text{Bi}_{1.6}\text{Sb}_{0.4}$	M0000SBT-2; Leg #1	14.2

The values for the pure compounds are considerably higher than those we had previously measured by the Powell method, and there can be no doubt that the new data are more accurate. However, these are still quite low thermal conductivities by ordinary standards, and it is probable that the result found for Mg_3Bi_2 contains a substantial ambipolar diffusion component, so that the actual lattice thermal conductivity is lower. In any case, one would not use pure Mg_3Bi_2 as a power generating thermocouple material if it becomes semimetallic at 200°C . The proper approach would evidently be to make use of the large decrease in thermal conductivity which results from alloying the two compounds, selecting some composition which gives an optimum compromise between the large band gap of Mg_3Sb_2

and the higher carrier mobilities of Mg_3Bi_2 . It is unlikely that the particular alloy composition we happened to prepare in this program falls exactly on the minimum thermal conductivity in the Mg-Sb-Bi system, and further work should clearly be done to determine how the conductivity varies with alloy proportions.

CONCLUSIONS

On the basis of the high resistivities obtained in the last two batches of Mg_3Sb_2 , it may be concluded that the developments in preparation technique accomplished in this program provided the means of producing intrinsic material with reasonable reliability. The preliminary measurements on the compound at elevated temperatures have shown that Seebeck coefficient measurements on nearly intrinsic specimens in the 300 to 800°C range will provide the information necessary to determine whether the carrier mobilities are large or small. Although experimental difficulties prevented us from getting enough data for the purpose in the present program, our subsequent success in making measurements on Mg_3Bi_2 up to 700°C indicates that the techniques described above can also be used in a straightforward manner on Mg_3Sb_2 .

The room temperature thermal conductivity of intrinsic Mg_3Sb_2 has been found to be larger than we had believed, although it is still smaller than that of any of the accepted power generating thermoelectric materials. The same is true of Mg_3Bi_2 . On the other hand, the thermal expansion coefficients measured for the compounds indicate a large degree of anharmonicity in the interatomic forces, which should lead to a rapid decrease of the lattice thermal conductivity with increasing temperature. It has also been shown that alloying of the two materials is very effective in reducing the thermal conductivity, for an 80% Mg_3Bi_2 , 20% Mg_3Sb_2 alloy was shown to have a lower conductivity than either pure compound. It seems quite likely that alloy compositions with thermal conductivities below 10 milliwatts/cm°C would be turned up by a systematic study.

The fundamental electrical properties of Mg_3Bi_2 remain something of a puzzle, for the compound seems to display a mixture of semiconducting and semimetallic properties. Both p- and n-type samples have been obtained, but, in contrast to Mg_3Sb_2 , treatments such as zone melting and exposure to high temperature have little effect on the resistivity or the absolute value of the Seebeck coefficient, both of which remain abnormally low by semiconductor standards. The most plausible interpretation of the data obtained on the one specimen measured at elevated temperatures so far seems to be that the material is a semiconductor at room temperature but becomes semimetallic at about 200°C. It also appears likely that it again becomes a semiconductor in the structure transformation which occurs at 700°C.

The apparently semimetallic properties of Mg_3Bi_2 between 200 and 700°C make it unlikely that the pure compound will be useful as a thermoelectric material by itself. But its extensive solid solubility with Mg_3Sb_2 and the marked reduction in thermal conductivity obtained by alloying indicate that Mg_3Bi_2 will be an important component of any thermocouple system eventually based on this class of compounds. Moreover, it is probable that the Mg_3Sb_2 - Mg_3Bi_2 alloy system will provide materials with a continuous range of band gap energies. This may make the alloys useful in certain types of photoconductive devices. It is also possible

that alloys with a moderate proportion of Mg_3Sb_2 may have small enough thermal conductivities and large enough carrier mobilities to be useful in thermoelectric heat pumping even though their band gap energies may not be large enough for high-temperature power generation service.

RECOMMENDATIONS

The principal achievement of the program just concluded has been to develop methods of preparing the compounds and alloys in the Mg-Sb-Bi system with high enough purity and with proportions close enough to the stoichiometric compositions so that the carrier concentrations are small compared to the intrinsic carrier concentration of Mg_3Sb_2 at only moderately elevated temperatures. Adequate measurement techniques have been demonstrated for use on these materials, but so far only preliminary information has been obtained on their properties. In some respects this information has been discouraging; the thermal conductivities of the pure compounds have been found to be higher than we had believed, and the apparent semimetallic behavior of Mg_3Bi_2 makes it seem unlikely that this compound will ever be a useful thermoelectric material by itself. On the other hand, it has been found that Mg_3Sb_2 and Mg_3Bi_2 have an extensive mutual solubility, and that the thermal conductivities of the alloys can be expected to be lower than that of either pure compound over a significant composition range. By analogy with other semiconductor-semimetal systems, one would also expect the alloys to have band gaps covering most or all of the range from 0.82 ev. to 0 ev., or at least to the band gap energy of Mg_3Bi_2 if that compound should prove to be a semiconductor. In other respects the fundamental properties probably also vary in a quite regular manner as the alloy composition passes from one compound to the other, but it should be noted that in some semiconductor alloy systems the carrier mobility passes through a relative maximum.

Having come so far, we feel that the work should be carried on to its logical conclusion, by proceeding to make the measurements of fundamental properties which have now become possible. These should include work on Mg_3Sb_2 , Mg_3Bi_2 , and a representative selection of their alloys.

Future work on Mg_3Sb_2 should concentrate on the problem of determining the carrier mobilities and effective masses. From our experience in this program, we still believe that the high-temperature intrinsic Seebeck coefficients originally proposed for this purpose will be a feasible and reasonably direct method of doing this. At the purity levels attainable with available sources of the constituents, it appears that the temperature range in which intrinsic Seebeck coefficient values will occur in most samples begins at about 300°C. Measurements should be carried from that temperature up to the highest temperatures practicable, in order to provide an accurate determination of the mobility ratio from the derivative of the Seebeck coefficient with respect to $1/T$. It would also be very helpful to measure the Hall effect and electrical conductivity in the samples at low temperatures, where the extrinsic carrier concentrations are much larger than the intrinsic concentrations. These data would serve to determine the extrinsic carrier concentrations and low-temperature mobilities. From the temperatures at which the samples changed from extrinsic to intrinsic behavior one could also obtain an independent estimate of the carrier effective masses.

The principal questions about Mg_3Bi_2 are whether it is a semiconductor or a semimetal and whether it makes transitions from one type of behavior to the other. Here again, it will be desirable to make measurements at low temperatures, both to determine extrinsic carrier concentrations and to find out whether the material behaves as a semiconductor below room temperature. The high temperature properties are also important, however, in view of the possibility that the material becomes a semiconductor (or at least suddenly alters the relative positions of its valence and conduction bands) when the structure transformation occurs. Now that the means are at hand, the Seebeck coefficient, resistivity, and Hall constant should be measured from liquid nitrogen temperature (or, say, temperatures at least as low as 100°K) up to temperatures as near as possible to the melting point.

In the case of the alloys of the two compounds, the first need is obviously to conduct a systematic preliminary survey of how their properties vary with composition. From the thermoelectric point of view, the most immediately interesting properties are the thermal conductivities and carrier mobilities, for the relative variations of these two quantities determine whether any of the alloys can have higher figures of merit than the pure compounds. A series of alloys spanning the composition range in steps of about 10 mol % should be prepared, and solid solubility should be determined by metallography. For the homogeneous alloys, the room temperature thermal conductivities and low temperature resistivities and Hall coefficients should be measured. It is important to know the approximate carrier concentrations as a check on the thermal data, for some differences in thermal conductivity can result from the electronic contribution due to accidental doping. The low temperature measurements can also give a preliminary idea of the carrier mobilities. Moreover, it should be possible to get low-temperature mobilities for both carrier types, for it may be anticipated that the samples will be p-type as prepared, and they can be converted to n-type by exposure to magnesium vapor. Measurements of resistivity as a function of temperature should be made at elevated temperatures to find how the band gap energy varies with composition among those alloys which are semiconductors.

When these studies are complete, the stage will be set for more intensive investigation of the materials with the highest mobilities and lowest thermal conductivities, provided that the values found for these properties seem to indicate that a high thermoelectric figure of merit can be obtained. The high temperature thermal conductivities of the pure compounds should be measured as well as those of the most promising alloys, so that the temperature dependences can be compared. On the alloys, measurements of the electrical properties (Hall effect, resistivity, and Seebeck coefficient) should be made at elevated temperatures to define the fundamental properties. It will then be possible, provided that the materials still seem promising, to proceed with studies of doping methods and development of optimized thermoelectric materials.

APPENDIX A

Because this report is primarily a history of how we developed and verified methods of making satisfactory specimens by comparing the properties of differently prepared batches, references to the batch compositions and differences in processing are scattered throughout the text. It has therefore seemed best to concentrate all of the data on compositions, variations in preparation procedure, and as-prepared properties of the batches in one place for ready reference. This has been done in Tables 11, 12 and 13 on the following pages, where batches of Mg_3Sb_2 , Mg_3Bi_2 and alloys of the two are respectively listed.

All of the batches prepared in the program are listed, whether they were successful or not, and each table is arranged in chronological order. The composition of each batch is given in two ways, by listing the actual weights of the constituents used and also by giving a chemical formula. The formulae are given in a way intended to show up deviations from stoichiometry as clearly as possible, for example, the formula " $\text{Mg}_{3.0398}\text{Sb}_{2.0000}$ " in the first entry of Table 11 indicates that the batch contained 398 atoms of excess magnesium for every 10,000 molecules of Mg_3Sb_2 .

Where applicable, the properties measured on each batch as prepared are also listed. The measurements made routinely on each batch included density determinations on all four legs and room temperature Seebeck coefficient measurements at three points on each leg. In the case of Mg_3Bi_2 the resistivity was also measured at three points on each leg with the four-point probe instrument mentioned in the text. The non-stoichiometric Mg_3Sb_2 batches had to be measured over a single span on each leg because of the inadequacies of the instruments available early in the program; on the other hand, full resistance profiles were measured on all legs of the stoichiometric batches. Since there appear to have been real differences in doping levels between legs, and sometimes from point to point on the same leg, we have elected to give the ranges of values found for the properties rather than the averages. Densities are similarly presented because it is probable that the observed spread of values is principally due to small amounts of void volume in the samples.

TABLE 11 CHARACTERISTICS OF MAGNESIUM ANTIMONIDE BATCHES

Batch Number and Formula	Batch Composition	When and How Prepared	Properties as Prepared
M3905S-1 $Mg_{3.0398}Sb_{2.0000}$	11.3808 gm. Mg* 37.4977 gm. Sb	11/11/65: Argon-filled stainless steel bomb; failed by leakage of charge from graphite crucible.	No measurements.
M3905S-2 $Mg_{3.0398}Sb_{2.0000}$	11.1962 gm. Mg* 36.8895 gm. Sb	11/22/65: Argon-filled stainless steel bomb; failed by contact of graphite with steel at 1250°C	No measurements.
M3905S-3 $Mg_{3.0398}Sb_{2.0000}$	11.2452 gm. Mg* 37.0509 gm. Sb	11/25/65: Argon-filled stainless steel bomb; successful.	S = -226 to -358 $\mu\text{V}/^{\circ}\text{C}$ ρ = .049 to .125 ohm cm Density: 4.021 to 4.022 gm/cm ³
M5051S-1 $Mg_{3.0505}Sb_{2.0000}$	10.8946 gm. Mg* 35.7700 gm. Sb	1/11/66: Evacuated stainless steel bomb; successful	S = -383 to -446 $\mu\text{V}/^{\circ}\text{C}$ ρ = .085 to .242 ohm cm Density: 3.905 to 4.034 gm/cm ³
M5051S-2 $Mg_{3.0505}Sb_{2.0000}$	11.4258 gm. Mg* 37.5140 gm. Sb	2/14/66: Graphite crucible previously saturated with Mg vapor at 900°C, in evacuated stainless steel bomb; possible leak in pinchoff tube.	S = -372 to -545 $\mu\text{V}/^{\circ}\text{C}$ ρ = .47 to .98 ohm cm Density: 3.843 to 4.022 gm/cm ³
M0000SD $Mg_{3.2630}Sb_{2.0000}$ $Mg_{3.0000}Sb_{2.0000}$	$\left\{ \begin{array}{l} 8.6216 \text{ gm. Mg}^* \\ 26.4610 \text{ gm. Sb} \end{array} \right.$ $\left\{ \begin{array}{l} 8.1319 \text{ gm. Mg}^* \\ 27.1484 \text{ gm. Sb} \end{array} \right.$	4/22/66: Double batch made in tandem crucible, in evacuated stainless steel bomb; successful.	$\left\{ \begin{array}{l} S = -227 \text{ to } -524 \mu\text{V}/^{\circ}\text{C} \\ \text{Density: } 3.976 \text{ gm/cm}^3 \end{array} \right.$ $\left\{ \begin{array}{l} S = -169 \text{ to } -342 \mu\text{V}/^{\circ}\text{C} \\ \text{Density: } 3.969 \text{ gm/cm}^3 \end{array} \right.$

* Dow Grade 5 magnesium

TABLE 11 (continued)

Batch Number and Formula	Batch Composition	When and How Prepared	Properties as Prepared
M5051ST-1 Mg ₃ .0505Sb ₂ .0000	11.1818 gm. Mg* 36.7124 gm. Sb	4/25/66: Argon-filled tantalum can in argon-filled stainless bomb; failed by controller malfunction.	No measurements.
M5051ST-2 Mg ₃ .0505Sb ₂ .0000	11.1795 gm. Mg* 36.7053 gm. Sb	4/25/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful.	S = -291 to -433 $\mu\text{V}/^{\circ}\text{C}$ ρ = .082 to .094 ohm cm Density: 3.995 to 4.013 gm/cm ³
M0000ST-1 Mg ₃ .0000Sb ₂ .0000	9.5002 gm. Mg [†] 31.7164 gm. Sb	6/2/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful	S = +256 to +559 $\mu\text{V}/^{\circ}\text{C}$ ρ = 2.26 to 9.69 ohm cm Density: 3.990 to 4.006 gm/cm ³
M0000ST-2 Mg ₃ .0000Sb ₂ .0000	9.6021 gm. Mg [†] 32.0566 gm. Sb	8/18/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful	S = +141 to -720 $\mu\text{V}/^{\circ}\text{C}$ ρ = 567 to 1545 ohm cm Density: 4.029 to 4.040 gm/cm ³
M0000ST-3 Mg ₃ .0000Sb ₂ .0000	9.4956 gm. Mg [†] 31.7011 gm. Sb	10/10/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful	S = +649 to -326 $\mu\text{V}/^{\circ}\text{C}$ ρ = 62 to 249 ohm cm Density: 4.024 to 4.034 gm/cm ³

* Dow Grade 5 magnesium

† Vacuum cast redistilled magnesium

TABLE 12 CHARACTERISTICS OF MAGNESIUM BISMUTHIDE BATCHES

Batch Number and Formula	Batch Composition	When and How Prepared	Properties as Prepared
M6714B-1 Mg ₃ .0679Bi ₂ .0000	9.0870 gm. Mg* 50.9212 gm. Bi	11/18/65: Argon-filled stainless steel bomb; possible leak during pinchoff, otherwise apparently successful	S = -67 to -93 $\mu\text{v}/^\circ\text{C}$ $\rho = .645$ to $.968 \times 10^{-3}$ ohm cm Density: 5.722 to 5.778 gm/cm ³
M3778B-1 Mg ₃ .0378Bi ₂ .0000	9.0488 gm. Mg* 51.2092 gm. Bi	1/10/66: Argon-filled stainless bomb, some of charge escaped from graphite crucible.	S = -61 to -97 $\mu\text{v}/^\circ\text{C}$ $\rho = .686$ to $.844 \times 10^{-3}$ ohm cm Density: 5.834 to 5.853 gm/cm ³
M5344B-1 Mg ₃ .0534Bi ₂ .0000	8.5135 gm. Mg* 47.9331 gm. Bi	2/24/66: Evacuated stainless bomb, graphite crucible impregnated with pyrolytic graphite; successful.	S = +15 to +91 $\mu\text{v}/^\circ\text{C}$ $\rho = .694$ to 1.425×10^{-3} ohm cm Density: 5.709 to 5.758 gm/cm ³
M0000BT-1 Mg ₃ .0000Bi ₂ .0000	7.8932 gm. Mg† 45.2320 gm. Bi	6/29/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful.	S = +39 to +41 $\mu\text{v}/^\circ\text{C}$ $\rho = .388$ to $.488 \times 10^{-3}$ ohm cm Density: 5.892 to 5.894 gm/cm ³
M0000BT-2 Mg ₃ .0000Bi ₂ .0000	8.3909 gm. Mg† 48.0841 gm. Bi	9/22/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful.	S = +39 to +45 $\mu\text{v}/^\circ\text{C}$ $\rho = .405$ to $.667 \times 10^{-3}$ ohm cm Density: 5.896 to 5.901 gm/cm ³

* Dow Grade 5 magnesium

† Vacuum cast redistilled magnesium

TABLE 13 CHARACTERISTICS OF MAGNESIUM ANTIMONIDE-MAGNESIUM BISMUTHIDE ALLOY BATCHES

Batch Number and Formula	Batch Composition	When and How Prepared	Properties as Prepared
M0000SBT-1 Mg ₃ .0000Sb _{.2000} Bi _{.8000}	8.2702 gm. Mg [†] 2.7611 gm. Sb 18.9571 gm. Bi	9/12/66: Argon-filled tantalum can in argon-filled stainless bomb; successful synthesis, but error in weights of elements	Two-phase sample; no valid measurements
M0000SBT-2 Mg ₃ .0000Sb _{.4000} Bi _{.6000}	8.3783 gm. Mg [†] 5.5943 gm. Sb 38.4095 gm. Bi	9/22/66: Argon-filled tantalum can in argon-filled stainless steel bomb; successful	S = + 58 $\mu\text{v}/^\circ\text{C}$ $\rho = 1.496 \times 10^{-3} \text{ ohm cm}$ Density: 5.347 gm/cm ³

† Vacuum cast redistilled magnesium

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ABSTRACT

An experimental study was made of the preparation and properties of Mg_3Sb_2 and Mg_3Bi_2 to determine their potential as thermoelectric materials. Methods of preparing pure, stoichiometric samples were successfully developed, but time and funds permitted high-temperature electrical property measurements on only one sample of each compound. Satisfactory measurement methods were found, and it appears that Mg_3Bi_2 is probably a semimetal at high temperatures and a semiconductor at low temperatures. However, the data were insufficient for a final conclusion on thermoelectric applications. The compounds' room temperature thermal conductivities were measured, and it was found that an alloy with the formula $\text{Mg}_3\text{Sb}_{0.4}\text{Bi}_{1.6}$ had a lower thermal conductivity than either pure material.